

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

NASA CR-

151472

Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Aircraft and Spacecraft

FINAL REPORT

by

John Gagliani
U.A.K. Sorathia
A.L. Wilcoxson

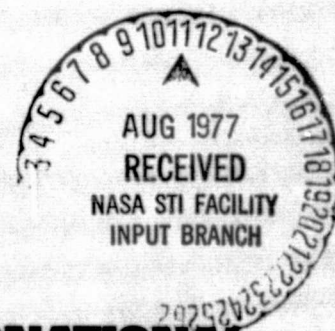
for

**National Aeronautical & Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058**

(NASA-CR-151472) DEVELOPMENT OF
FIRE-RESISTANT, LOW SMOKE GENERATING,
THERMALLY STABLE END ITEMS FOR AIRCRAFT AND
SPACECRAFT Final Report (Solar Turbines
International) 130 p HC A07/MF A01 CSCL 11G G3/27

N77-28301

Unclas
39234



SOLAR TURBINES INTERNATIONAL

An International Harvester Group 2200 Pacific Highway, P.O. Box 80966, San Diego, California 92138

Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Aircraft and Spacecraft

FINAL REPORT

by

John Gagliani
U.A.K. Sorathia
A.L. Wilcoxson

for

**National Aeronautical & Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058**

NOTICE

This document is a report of data and findings of an investigation. Either investigation and/or optimization may result in verification, supplemental information, change, correction or deletion of any or all areas of this report. The fact that the Government and the writers may have formulated, furnished or in any way supplied the information and data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Neither the writers nor the U.S. Government nor any person acting on behalf of the Government or writers

(A) makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned patent rights; or

(B) assume any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

SOLAR TURBINES INTERNATIONAL
An International Harvester Group 2200 Pacific Highway, P.O. Box 80966, San Diego, California 92138

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1	1
PROGRAM SCOPE AND OBJECTIVE	
2	5
BACKGROUND AND PROGRAM APPROACH	
3	11
EXPERIMENTAL PROCEDURES	
3.1 Selection of Raw Materials	11
3.2 Purification of Raw Materials	11
3.3 Synthesis of Liquid and Powder Polyimide Precursors	12
3.3.1 Monomeric Liquid Precursor - 160 Series	12
3.3.2 Copolyimide Foam Precursor - 160 Series	13
3.3.3 Monomeric Liquid Precursor - 170 Series	13
3.3.4 Copolyimide Foam Precursor - 170 Series	14
3.3.5 Monomeric Liquid Precursor - 190 Series	14
3.3.6 Copolyimide Foam Precursor - 190 Series	14
3.3.7 Synthesis and Processing of Final Candidates	14
3.3.8 Reactions; Esterification, Amidization, Imidization	15
3.4 Flexible Resilient Polyimide Foams	16
3.5 Laminate Floor and Wall Paneling	21
3.6 Thermal Acoustical Insulation Material	26
3.7 High Strength Polyimide Molded Shapes	27
3.8 Flexible Polyimide Coated Fabrics	28
4	33
EXPERIMENTAL RESULTS	
4.1 Flexible Resilient Polyimide Foams	33
4.1.1 Advanced Polyimide Synthesis	33
4.1.2 Foaming Studies	49
4.1.3 Scale-up Processes	50
4.1.4 Characterization of the Candidate Polyimide Foam	60
4.1.5 Fabrication of Samples for Submittal to NASA- LBJ Space Center	71
4.2 Laminate Floor and Wall Paneling	71
4.2.1 Tooling	71
4.2.2 Resin and Reinforcement Study	72
4.2.3 Process Parameters/Panel Configuration	84
4.2.4 Specimen Preparation and Screening	92
4.2.5 Advanced Testing	94
4.2.6 Fabrication of Samples for Submittal to NASA- LBJ Space Center	94
4.2.7 Specimen Preparation and Screening	97
4.2.8 Fabrication of Wall Panel Samples for Submittal to NASA-LBJ Space Center	98

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
4.3 Optimization and Characterization of Thermal-Acoustical Insulation	98
4.3.1 Advanced Polyimide Synthesis	99
4.3.2 Foaming Studies and Preliminary Testing	101
4.3.3 Preparation of Thermal Acoustical Insulation Materials and Selection of Candidates	102
4.3.4 Final Characterization of Thermal Acoustical Insulation Material	104
4.3.5 Fabrication of Large Samples for Submittal to NASA-LBJ Space Center	104
4.4 Investigation of Processes for High Strength Polyimide Molded Shapes	
4.4.1 Selection of Polyimide Precursors and Resin Reinforcements	106
4.4.2 Preparation and Evaluation of Molding Hardware	108
4.4.3 Prototype Molded Shapes by Compression Techniques	111
4.4.4 Investigation of Methods to Produce Decorative Surface Effects	111
4.4.5 Advanced Testing	112
4.4.6 Fabrication of Molded Samples for Submittal to NASA-LBJ Space Center	112
4.5 Optimization of Flexible Polyimide Coated Fabrics	113
4.5.1 Evaluation of Fabrics	113
4.5.2 Investigation of Decorative Effects	115
4.5.3 Preparation of Coated Fabrics for Testing	115
4.5.4 Fabrication of Samples for Submittal to NASA-LBJ Space Center	117
5 RECOMMENDATIONS FOR FUTURE WORK	119
REFERENCES	121

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Program Schedule	2
2	Program Flow Diagram	4
3	High Intensity Heat Test	6
4	Microwave Oven Gerling Moore Model 4110	18
5	Thermex Heater, Model CP40-B Chemetron Corp.	18
6a	Foaming by Thermal Processes (FR-160-2)	19
6b	Foaming by Vacuum Processes (FR-170-1)	19
7a	Meker Burner Test - 1 Minute Exposure	20
7b	Meker Burner Test - 5 Minutes Exposure	20
7c	Meker Burner Test - 10 Minutes Exposure	21
8	NBS Smoke Density Chamber	22
9	Flexible Resilient Foam - Fatigue Tester	23
10	Preparation of Rigid Panels From Short Graphite Fibers	23
11	Preparation of Rigid Panels From Continuous Mat Materials	25
12	Carbon Mat Filled Floor Panel Resin E-160-5	25
13	Burn Test	26
14	Bruel and Kjaer Standing Wave Apparatus Type 4002	27
15	Izod Tester	29
16	Izod Test Specimen	29
17	Tensile Specimens; Molded Glass Filled 170-2 Compositions	30
18	Rockwell Hardness Tester. Molded Test Sample	30
19	Polyimide Coated Fabrics	31
20a	Before the Humidity Test	35
20b	After 72 Hours in Humidity Test	35
20c	After 7 Days in Humidity Test	35
21	Density Profile of Flexible Polyimide Foams	40
22a	Polyimide Foam. FR 170-1 - Untested	42
22b	Polyimide Foam FR 170-1 After 7 Days at 73.9°C (165°F) and 100% RH	42

LIST OF ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
23	Polyimide Foams, 2,6DAP:MDA System. Effect of Heterocyclic Diamine Concentration on Foam Rise and Cellular Structure	43
24	Polyimide Foams. Effect of Aromatic Diamine on Foam Rise. Cellular Structure and Rigidity	45
25	Esterifying Agents, Effect on Foam Properties	47
26	FSB Surfactant; Effect of Concentration on Density of Flexible Resilient Foams (FR 170-1)	49
27	L-170 Additives; Effect of Concentration on Foam Density (FR 170-1)	49
28	B-Staging Temperature; Effect on Residual Volatiles of 170-1 Polyimide Precursors	52
29	Time-Temperature; Effect on Volatile Content of 170-1 Foaming Resin Processed at Reduced Pressure	54
30	Multi-Stage Foaming; Effect of Pressure on Density (FR 170-1)	57
31	Foaming by Vacuum Processes (FR 170-1)	58
32	Foaming by Thermal Processes, FR 170-1	58
33a	Resilient Polyimide Foam by Microwave Foaming (170-2)	61
33b	Thermal Acoustical Polyimide Foam by Microwave Foaming (170-2, 0.2% FSB)	61
34	Multi-Stage Technique; Foaming Behavior of Precursors With Decreasing 2,6DAP Molar Ratio	65
35	Microwave Foaming; Effect of Preheat Temperature on Density (FR 170-1)	66
36	Microwave Foaming; Effect of FR 170-1 Precursor Thickness on Foam Rise with Pre-Heat Cycle	67
37	Microwave Foaming; Effect of FR 170-1 Precursor Thickness on Foam Rise Without Pre-Heat Cycle	67
38	Compressive Strength of 160 Series Resins Filled With Chopped Carbon Mat	73
39	Compressive Strength of 170 Series Resins Filled With Chopped Carbon Mat	74
40	Compressive Strength of 190 Series Resins Filled With Chopped Carbon Mat	74
41	Compressive Strength of 170-2 Resins Filled With Various Reinforcements	76
42	Compressive Strength of 170-3 Resins Filled With Various Reinforcements	76

LIST OF ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
43	Compressive Strength of 160-3 Resins Filled With Various Reinforcements	77
44	Compressive Strength of 190-2 Resins Filled With Various Reinforcements	77
45	Filler Concentration; Effect on Compressive Strength of 160-5 Filled Resins	79
46	Effect of Loading on Compressive Strength of 160-5 Filled Resins	80
47	Polyimide Foam Filled Honeycomb	81
48	Polyimide Foam Filled Honeycomb	81
49	Polyimide Rigid Panel - New Configuration	82
50	Polyimide Rigid Panel - New Configuration	82
51	Polyimide Rigid Panel - New Configuration	83
52	Surfactants, Effect on Compressive Strengths of 160-5 Filled Resins	85
53	Surfactants, Effect on Compressive Strength of 170-2 Filled Resins	86
54	L-170 Additive, Effect on Compressive Strength of 160-5 Filled Resins	86
55	Processing Parameter; Effect on Compressive Strength of Rigid Panels (170-2)	88
56	Drying Temperature; Effect on Compressive Strength of Rigid Panels (170-2)	88
57	Resin Additions; Effect on Compressive Strength of Rigid Panels (170-2)	89
58a	Carbon Mat Reinforced Rigid Foam Panels; E 170-2	95
58b	Foamed Filled Honeycomb Panels; FR 160-5	95
58c	Chopped Glass Strands Reinforced Rigid Foam Panels; E 170-2	96
59	Floor Panels	96
60	Wall Panels	98
61	Fillers; Effect on Density of 160-0 Foaming Resin Modified with 0.2% FSB	100
62	FR 160-0 Foamed on Fiberglass Batting	101
63	Density; Effect on Impact Strength of 160-5 Nomex Molded Shapes	109
64	Mold Configuration	110
65	Coated Asbestos Fabric	116

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I Oxygen Index of Flexible Resilient Foams	7
II Specific Optical Density of Flexible Resilient Foams	7
III Diamines and Dianhydrides and Their Properties	9
IV Re-Evaluation of Polyimide Foams for Hydrolytic Stability at 73.9°C and 100% RH	34
V Advanced Polyimide Foam Precursors and Foam Characteristics Effect of Mole Ratio, Excess Reactants, and Esterifying Agent	36
VI Properties of Flexible Foams With Surface Active Agents	38
VII Study of Foaming Agents and Additives	39
VIII 160 Series; Hydrolytic Stability of Polyimide Foams at 73.9°C and 100% RH	41
IX 170 Series; Hydrolytic Stability of Polyimide Foams at 73.9°C and 100% RH	42
X 190 Series; Hydrolytic Stability of Polyimide Foams at 73.9°C and 100% RH	46
XI Selection of Candidates	50
XII Effect of Reaction Temperature on FR-170-1	52
XIII Polyimide Foam Precursors With Improved Reaction Conditions	55
XIV Multi-Stage Foaming; Effect of Surfactant Concentration on Polyimide Foams Derived from FR 170-1	57
XV Thermal Foaming of 170-1 Resin Mass and Thickness Effect	62
XVI Thermal Foaming of 170-1 Resin; Temperature Effect	62
XVII Effect of Pressure on the Foaming Behavior of FR 170-1	64
XVIII Surfactants; Effect on Density and Resiliency of Foams Derived from 170-1 Precursors by Microwave Heating	64
XIX Surfactants; Effect on Density and Resiliency of Foams Derived From 170-2 Precursors by Microwave Heating	68
XX Raw Material Cost of Final Candidates 170-1 and 170-2	69
XXI Flexible, Resilient Foams: Final Screening of Candidates	69
XXII Summary of Results. Flexible Resilient Foams 170-1 Resin	70

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
XXIII	Rigid Panels; Effect of Glass Strands Concentration on Properties	84
XXIV	FC-430 Surface Active Agent Concentration; Effect on Compressive Strength (E 170-2)	90
XXV	Floor Panels; Selection of Liquid Resin System	93
XXVI	Absorption Coefficient of Foams Derived From 160-0 Precursors	103
XXVII	Absorption Coefficient of Foams Derived From 170 Precursors	103
XXVII	Summary of Results. Thermal Acoustical Insulation 170-2 Resin 0.2% FSB	105
XXIX	Izod Impact Strength of Molded E 170-2 Compositions	107
XXX	Nomex, Effect of Concentration on Impact Strength of Molded E 160-5 Compositions	107
XXXI	Chopped Glass Strands; Effect of Concentration on Properties of Molded E 170-2 Compositions	108
XXXII	Density; Effect on Impact Strength of 160-5 Nomex Molded Shapes	110
XXXIII	Summary of Results - Molded Shapes	112
XXXIV	Coated Fabrics - Coating Physical Properties	114
XXXV	Summary of Results - Coated Fabrics	117

1

PROGRAM SCOPE AND OBJECTIVES

This program has been devised to provide cost effective pilot plant scale processes for producing fire-resistant, low-smoke emitting, flexible, resilient, open cell polyimide foams for use as seat cushions in commercial aircraft and spacecraft. The technology used for producing the flexible resilient foams has been adapted to fabricate other cellular materials with a wide spectrum of density and rigidity for use in a variety of aircraft applications including thermal/acoustical insulation, flooring materials, wall paneling and molded hardware. Additionally, the program has been organized to provide optimized processes for producing fire hardened, thermally stable coated fabrics to upgrade the performance of interior aircraft hardware.

A principal objective of this program was to obtain improvement of these aircraft interior materials by modification of existing polymer structures, by refinement of process parameters and by the use of mechanical configurations designed to overcome specific deficiencies. Unlike existing cellular materials, the materials developed within the scope of this program have been formulated to possess three important attributes:

1. Inherent nonburning characteristics.
2. No discernible smoke formation upon combustion.
3. No detectable toxic by-products of combustion.

Solar, during the past eleven years, has developed polyimide compositions that have been processed by compression molding into frictional and mechanical components for use in small gas turbine engines of which we are a major manufacturer. These same resins have been further studied in this program to offer a solution to the problem of flammability of conventional aircraft materials.

The polyimide materials evaluated under this program are fire-resistant, low-smoke emitting open-cell foams for use in five different types of aircraft cabin structures. These include: resilient foams, laminate floor and wall paneling, thermal/acoustical insulation, molded shapes, and coated fabrics. All five have been produced from essentially the same polyimide precursor and have resulted in significant benefits from transfer of technology between the various tasks.

This program consists of five phases describing the general objectives and the work plan for optimizing, selecting, and fabricating each of the different types of aircraft structures. The work plan constituting the various tasks of the Program Schedule shown in Figure 1.

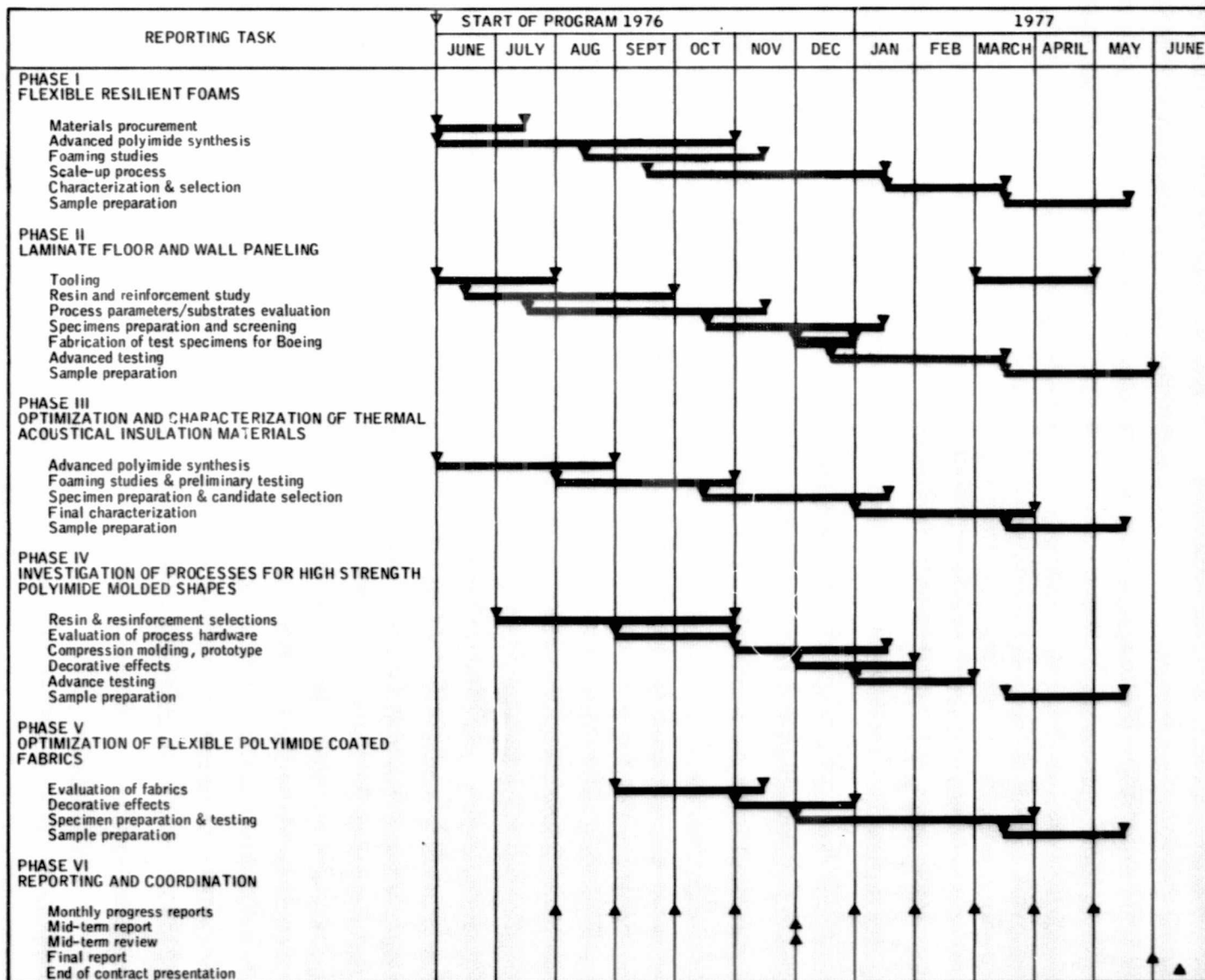


Figure 1. Program Schedule

- Phase I concerns itself with a re-evaluation of the most promising flexible resilient polyimide foams developed under NAS9-14718, NASA-LBJ Space Center, followed by advanced polyimide synthesis, in order to define the factors which contribute to the critical properties known not to be up to normal standard, namely, humidity and fatigue characteristics.
- Phase II entails development of technology for fabrication of laminate floor and wall paneling and involved considerable transfer of technology from Phase I since the rigid foams were produced from essentially the same liquid precursors used in the preparation of the powder foam resins. In addition, new mechanical concepts of panel construction have been evaluated which include among others foam filled honeycomb core structures.
- Phase III covers the development of low density polyimide foams possessing suitable acoustical attenuation and flame retardation characteristics and involved complete transfer of technology from Phase I of the program, since thermal-acoustical foams have been produced from essentially the same polyimide foam precursors used in preparation of the flexible resilient foams. Modification of conventional fiberglass acoustical materials with polyimide coatings or foam sheets to enhance the fire impingement properties of the glass has also been attempted.
- Phase IV covers investigation of techniques and process parameters for heat forming rigid polyimide foams into useful shapes to replace conventional, more flammable plastics. This phase of the program has resulted in considerable transfer of technology from the data developed in the study of rigid panels.
- Phase V covers the optimization and characterization of flexible polyimide coated fabrics to obtain decorative effects of fire hardened aircraft interior hardware.

The interrelations between the various tasks are shown in the Flow Diagram (see Fig. 2). The overall technical content of the program was scheduled to cover a period of 12 months starting from June 1, 1976. A two month extension of the period of performance and final delivery of material was requested and the extension approved by NASA-LBJ Space Center. This request was the result of efforts expended for additional candidate materials for evaluation under this program. All these efforts were performed at no additional cost.

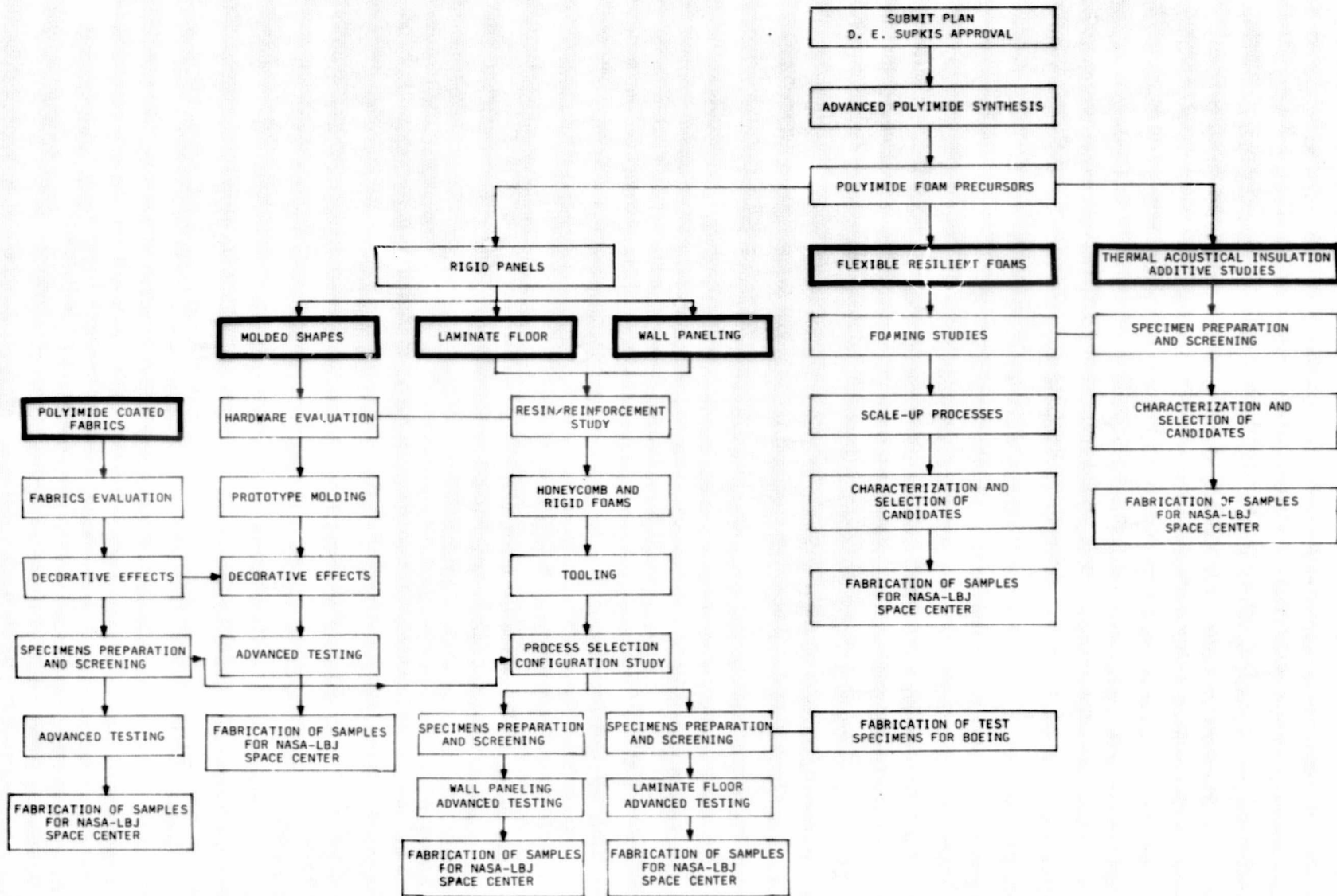


Figure 2. Program Flow Diagram

2

BACKGROUND AND PROGRAM APPROACH

The technology for synthesizing conventional cellular materials has been available for many years and a large number of highly flexible and rigid foams have been developed to satisfy increased market application. Modifications of the polymers have also been carried out by addition of flame retardant or by reactive additives to produce materials with self-extinguishing characteristics. The many efforts to make conventional foams fire retardant have adversely increased the hazard to personnel, since, once ignited, these foams release large quantities of smoke and toxic products which are often the major cause of death.

Advanced approaches to the flammability problem of plastic materials have been devised at Solar Research Laboratories. Instead of modifying an existing polymer, Solar has developed a new family of polymers possessing intrinsic non-flammable properties. The non-burning plastic material developed at Solar is a new polyimide polymer which possesses fire hardening properties and does not produce detectable quantities of smoke or toxic fumes upon combustion. These properties are evidenced by the intumescent behavior and by the carbonaceous surface layer of protective char formed when the material is subjected to fire tests. The fire hardening properties of the polyimide foams developed at Solar are demonstrated in Figure 3. The combustion characteristics are shown in Table I and II where the Oxygen Index (LOI) and the Specific Optical Density (D_s) of the flexible resilient foams are reported.

The program approach is based upon investigation and optimization of the properties of these polyimide materials for use in five different types of aircraft cabin structures. These include:

- Resilient foams
- Laminate floor and wall paneling
- Thermal/Acoustical Insulation Foams
- Molded Shapes
- Coated Fabrics

Since the first four were produced from essentially the same polyimide resin precursor, the proposed program was organized to proceed with investigation of all four forms concurrently, or as closely as possible. This approach has been possible due to the adaptability of the candidate resins to processing in a wide variety of forms.

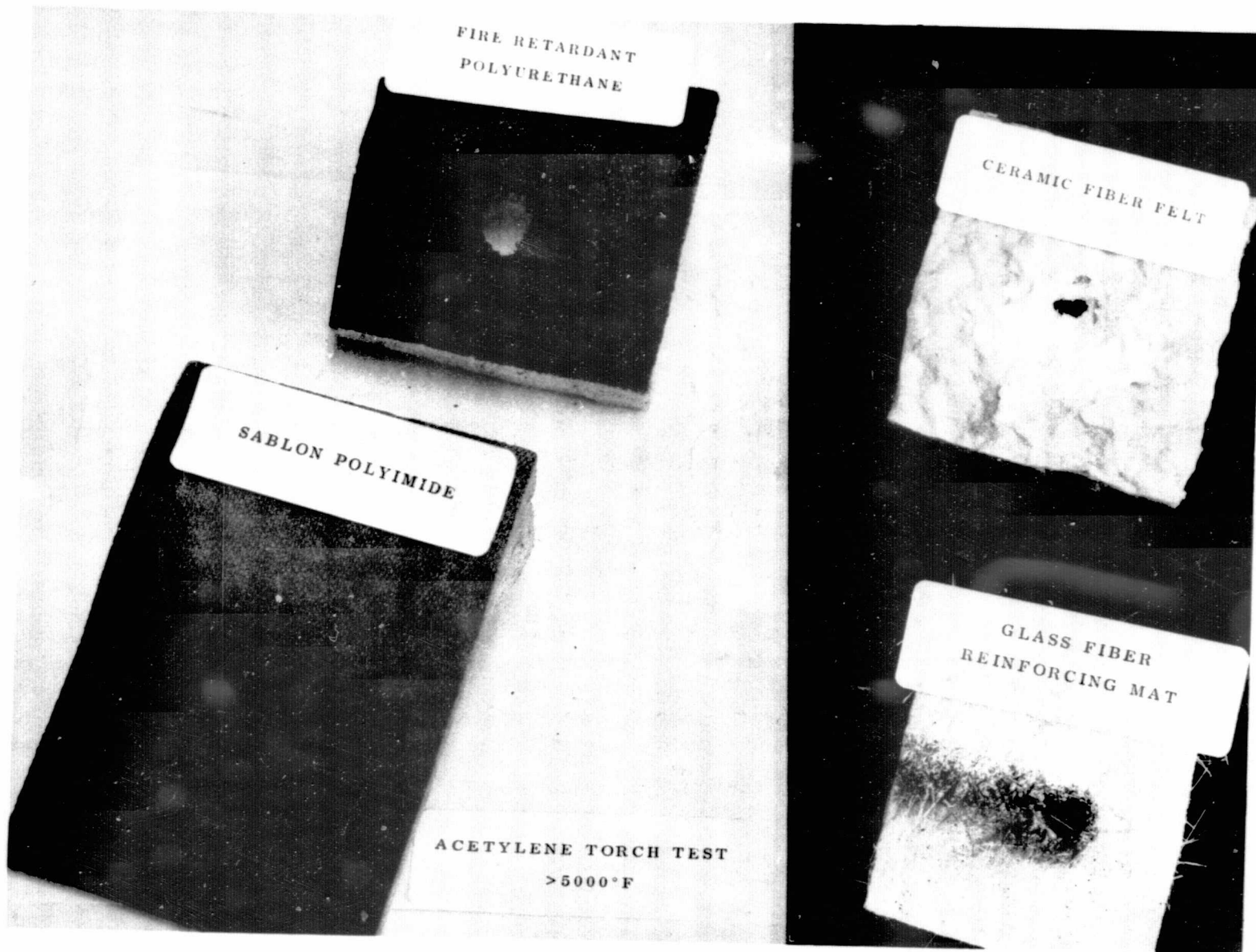


Figure 3. High Intensity Heat Test

Table I
Oxygen Index of Flexible Resilient Foams

	LOI
<u>Resin No. 25</u>	
F-445	44
F-394	43
F-314	42
F-399	44
F-412	46
Average	43.8
<u>Resin No. 29</u>	
F-372	44
F-403	45
F-424	42
F-396	46
F-386	45
Average	44.4

Table II
Specific Optical Density of Flexible Resilient Foams

	D _s Condition	
	Smoldering	Flaming
<u>Foam No. 25</u>		
F-394	0	0
F-395	0	0
F-395	0	0
Average	0	0
<u>Foam No. 29</u>		
F-416	1.1	0.5
F-416	1.0	0.7
F-416	0.8	0.4
Average	1.0	0.5

The largest portion of the proposed program has been expended on optimization of resilient polyimide foams intended for use as seat cushions. While a significant effort has already been devoted to this task (Ref. 1), resilient foams are the most difficult of polyimide products to produce. The samples produced in the referenced program were significantly deficient in at least three areas: fatigue strength, resistance to high humidity (steam) conditions, and production costs. Furthermore the major emphasis of this proposed task has been in the correction of these deficiencies and included synthesis of new foam precursors and evaluation of foam processes capable of affording homogeneous cellular structure by economical methods.

The concepts of rigid panel construction evaluated in this program included: rigid polyimide foamed on suitable substrates, polyimide filled honeycomb structures, and new configurations for floor and wall paneling. Primary objectives have been the providing of adequate mechanical strength and fire hardened properties. Optimization has proceeded in iterative steps of sample preparation, testing, modification, and improvement.

The development of thermal acoustical insulation was expected to define but not necessarily optimize the techniques for production of polyimide foams for this application. Primary testing criteria have been the optimum performance of the material in flame retardation, acoustical attenuation, and wicking. The study for the selection of the polyimide precursor and inert fillers has constituted a major portion of this task. Modification of conventional fiberglass battings has also been undertaken to improve the thermal characteristics of these materials owing to their poor flame impingement properties.

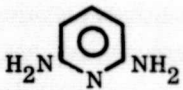
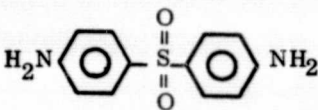
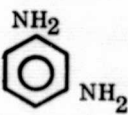
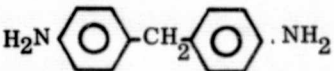
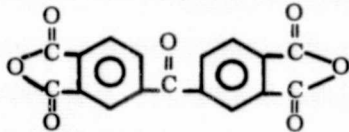
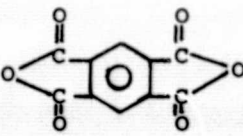
The development of high strength polyimide molded shapes has been undertaken with major emphasis on defining the process conditions which yield denser foam structures. The economics of producing rigid high density polyimide foam shapes, as opposed to the more conventional ABS plastics, have been expected to be a deterrent to widespread use. The advantages in safety are such, however, that reasonable effort to achieve a viable, economical process has been given serious considerations.

The last task covered the use of polyimide resin compositions and development of process parameters to fabricate flexible, coated fabrics possessing fire hardened properties. Glass and synthetic fabrics have been evaluated and screened to select an optimum material on the basis of mechanical, physical and thermal properties.

These products have been produced based upon prior Solar Research Laboratory technology. This technology is based upon the reaction of at least one heterocyclic diamine and at least one aromatic diamine with an aromatic tetraacid possessing low dissociation constants. These reactants have been proven to yield polyimide foams with a wide range of properties from which to select candidates for a variety of applications.

The diamines and dianhydride utilized in this program and their relevant physical properties are given in Table III. These reactants have been selected on the basis of their availability, cost and on their ability to yield foams possessing a wide range of physical and mechanical properties.

Table III
Diamines and Dianhydrides and Their Properties

Diamines/Dianhydride	Structure	Melting Point
2,6 Diaminopyridine		120-122°C (248-252°F)
4,4' Diaminodiphenylsulfone		176-177°C (349-351°F)
meta Phenylenediamine		62-63°C (144-145°F)
Methylenedianiline		93-94°C (199-201°F)
Benzophenone 3,3',4,4' Tetracarboxylic acid dianhydride		224-226°C (435-439°F)
Pyromellitic Dianhydride		283-286°C (541-457°F)

3

EXPERIMENTAL PROCEDURES

This section outlines the experimental and test procedures and includes selection of raw materials (Section 3.1), purification of raw materials (Section 3.2), synthesis of copolyimide precursors (Section 3.3) and description of fabrication procedures, tests and test facilities for the products outlined in the sequence: flexible resilient foams (Section 3.4), laminate floor and wall paneling (Section 3.5), thermal acoustical insulation (Section 3.6), high strength polyimide molded shapes (Section 3.7) and polyimide coated fabrics (Section 3.8).

3.1 SELECTION OF RAW MATERIALS

The availability of a wide range of aromatic and aliphatic diamines and tetracarboxylic acid dianhydrides enables the mechanical and thermal properties of most polyimide resins to be varied within wide limits. However, for the type of polyimide materials under development in this program, the raw materials are limited to those reactants possessing low dissociation constants as it has been established under one or more of Solar's existing patents. As a result of these previous studies, the most promising diamines and dianhydrides are reported in Section 2, Table III together with their relevant physical properties. These materials are available in commercial quantities and are known to be non-toxic.

3.2 PURIFICATION OF RAW MATERIALS

- 2,6 Diaminopyridine - This highly purified diamine (MP 120-122°C, 248-252°F) was obtained from Reilly Tar & Chemical Co. and used without purification.
- 4,4'Diaminodiphenyl sulfone - This highly purified diamine (MP 175-176°C, 347-349°F) was obtained from Roussel Corp. and used without purification. The same material obtained from RSA Corp. (MP 171-173°C, 340-343°F) required recrystallization from isopropyl alcohol solutions before use.
- p-p'Methylene dianiline - This commercial grade diamine was obtained from Allied Chemicals Co. (MP 90-92°C, 194-197.6°F) and used without purification.

- m Phenylenediamine - This commercial grade diamine was obtained from Miller-Stephenson Chemical Co. and used without purification (MP 62-63°C, 143.6-145.4°F).
- Pyromellitic Dianhydride - This product was obtained from Aldrich Chemical (MP 283-286°C, 541-547°F) and used without purification.
- Benzophenone 3,3',4,4'-Tetracarboxylic acid dianhydride - This product was obtained from the Gulf Oil Co. Chemical Division. The off white material was slurried in warm acetone, washed and dried at 120°C (248°F) to yield a material (MP 225-226°C, 437-439.5°F) suitable for synthesis of polyimide precursors.
- Surface Active agents -
 - L-type surfactants were purchased from Union Carbide.
 - Zonyl FSB and FSC from E.I. Dupont de Nemours.
 - FC-430 and FC-431 from the 3M Co.
 - DC type surfactant from Dow Corning.
 - Victamide 511 from Witco Corporation
 All surfactants were used as received.
- Ethyl Alcohol, Mallinkrodt No. 7019
- Methyl alcohol, Mallinkrodt No. 3016
- n Propanol, Mallinkrodt No. 7169

3.3 SYNTHESIS OF LIQUID AND POWDER POLYIMIDE PRECURSORS

The following procedures are typical of those used to prepare liquid resin precursors and copolyimide foam precursors belonging to 160, 170, and 190 series. Final optimized procedures are given for those precursors selected as candidates for fabrication of the final products.

3.3.1 Monomeric Liquid Precursor - 160 Series

Benzophenone tetracarboxylic acid dianhydride (BTDA) (322.23 g, 1.0 mole) was added to 240 ml of 3A anhydrous ethyl alcohol and 24 ml of H₂O in a 1-liter 3 neck flask, equipped with thermometer, mechanical stirrer, and reflux condenser. After addition, the mixture was heated to reflux, and refluxed until clear. The mixture was then refluxed for an additional 60 minutes to ensure complete esterification of BTDA to its half-ester. It was then cooled to 50-60°C (122-140°F).

2,6Diaminopyridine, (2,6DAP) (27.28 g, 0.25 mole) and 4,4'diaminodiphenyl sulfone, (4,4'DADPS) (186.23 g, 0.75 mole) were added to the half-ester solution and the mixture refluxed at 91-93°C (195.8-199.4°F) for 30 minutes. The viscous solution was allowed to cool to 50-60°C (122-140°F) with agitation. Additives, if any, were added at this stage and the mixture agitated for an additional 45 minutes. The liquid resin was then transferred into two 30 x 30 x 1 cm (12 x 12 x 0.4 inch) aluminum dishes for further processing.

Modification of the chemical structure of the foams belonging to the 160 series have been made by varying the mole ratio of the heterocyclic diamine of the precursors, as will be discussed.

3.3.2 Copolyimide Foam Precursor - 160 Series

The monomeric liquid precursor was B-staged by heating the syrup in a circulating air oven at 82.2°C (180°F) for 12-16 hours, followed by drying in a vacuum oven at 76.7°C (170°F) for 90-120 minutes at a absolute pressure of 33.4-16.5 kPa (9.9-4.9 in. Hg). Thereafter, the solid prepolymer was crushed and pulverized into a powder having a maximum particle size of 297 microns (100% through 50 mesh screen) and used to prepare foam sheets.

3.3.3 Monomeric Liquid Precursor - 170 Series

Benzophenone tetracarboxylic acid dianhydride (BTDA) (322.23 g, 1.0 mole) was added to 240 ml of 3A anhydrous ethyl alcohol and 24 ml of H₂O in a 1-liter, 3 neck flask, equipped with thermometer, mechanical stirrer and reflux condenser. After addition, the mixture was heated to reflux and refluxed until clear. The mixture was then refluxed for an additional 60 minutes to ensure complete esterification of BTDA to its half ester. It was then cooled to 40-50°C (104-122°F). 2,6Diaminopyridine (2,6DAP) (54.56 g, 0.5 mole) and p-p'methylene dianiline (MDA) (99.13 g, 0.5 mole) were added to the half ester solution and the mixture heated at 65-70°C (149-158°F) for 30 minutes. The highly viscous solution was allowed to cool to 50-60°C (122-140°F) with agitation. Additives, if any, were added at this stage and the mixture agitated for an additional 45 minutes. The liquid resin was then transferred into two 30 x 30 x 1 cm (12 x 12 x 0.4 in.) aluminum dishes for further processing.

Modification by chemical structure of the foams belonging to 170 series have been made by varying the mole ratio of the heterocyclic diamine of the precursor as will be discussed.

3.3.4 Copolyimide Foam Precursor - 170 Series

The monomeric liquid precursor was B-staged by heating the syrup in a circulating air oven at 76.7°C (170°F) for 12-15 hours, followed by drying in a vacuum oven at 65.5°C (150°F) for 90-120 minutes at an absolute pressure of 33.4-16.5 kPa (9.9-4.9 in. Hg). Thereafter, the solid prepolymer was crushed and pulverized into a powder having a maximum particle size of 297 microns (100% through 50 mesh screen) and was used to prepare foam sheets.

3.3.5 Monomeric Liquid Precursor - 190 Series

Benzophenone tetracarboxylic acid dianhydride (BTDA) (322.23 g, 1.0 mole) was added to 240 ml of 3A anhydrous ethyl alcohol and 24 ml of H₂O in a 1-liter 3 neck flask, equipped with thermometer, mechanical stirrer, and reflux condenser. After addition, the mixture was heated to reflux and refluxed until clear. The mixture was then refluxed for an additional 60 minutes to ensure complete esterification of BTDA to its half-ester. It was then cooled to 40-50°C (104-122°F).

2,6Diaminopyridine, (2,6DAP) (54.56 g, 0.5 mole) and meta phenylene diamine (mPDA) (54.07 g, 0.5 mole) were added to the half ester solution and the mixture heated at 60-65°C (140-149°F) for 30 minutes. The highly viscous solution was allowed to cool to 50-55°C (122-131°F) with agitation. Additives, if any, were added at this stage and the mixture agitated for an additional 45 minutes. The liquid resin was then transferred into two 30 x 30 x 1 cm (12 x 12 x 0.4 in.) aluminum dishes for further processing.

3.3.6 Copolyimide Foam Precursor - 190 Series

The monomeric liquid precursor was B-staged by heating the syrup in a circulating air oven at 71.1°C (160°F) for 12-15 hours followed by drying in a vacuum oven at 65.5°C (150°F) at an absolute pressure of 33.4-16.5 kPa (9.9-4.9 in. Hg). Thereafter, the solid prepolymer was crushed and pulverized into a powder having a maximum particle size of 297 microns (100% through 50 mesh screen) and used to prepare foam sheets.

3.3.7 Synthesis and Processing of Final Candidates

Copolyimide Precursors 170-1 and 170-2

Benzophenone tetracarboxylic acid dianhydride (BTDA) (322.23 g, 1.0 mole) was added to 240 ml of 3A anhydrous ethyl alcohol and 24 ml of water in a 1-liter, 3 neck flask equipped with thermometer, mechanical stirrer, and reflux condenser. After addition, the mixture was heated to reflux and

refluxed until clear. The mixture was then refluxed for an additional 60 minutes to ensure complete esterification of BTDA to its half ester. It was then cooled to 40-50°C (104-122°F).

2,6Diaminopyridine (2,6DAP) (43.65 g, 0.4 mole for E-170-1 and 32.74 g, 0.3 mole for E-170-2) and p-p' methylene dianiline (MDA) (118.96 g, 0.6 mole for E-170-1 and 138.78 g, 0.7 mole for E-170-2) were added to the half ester solution and the mixture heated to 60-65°C (140-149°F) for 5 minutes. The highly viscous solution was cooled to 40-50°C (104-122°F) with a water bath. The liquid 170-2 precursor was used directly for preparation of molded polyimide shapes. Additives were added at this stage by addition of 0.91 g of FSB, a surface active agent, to modify the precursors for use in thermal-acoustical insulation or with 0.91 g of FC-430 and FC-431 for fabrication of floor and wall paneling. The mixture was agitated for an additional 45 minutes, and then used directly or transferred into two 30 x 30 x 1 cm (12 x 12 x 0.4 in.) aluminum dishes for further processing.

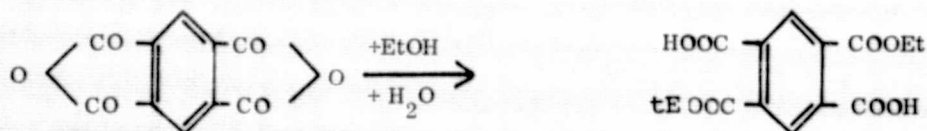
The liquid precursor was then B-staged by heating the syrup in a circulating air oven at 65.5°C (150°F) for 12-15 hours followed by drying in a vacuum oven at 65.5°C (150°F) for 90-120 minutes at an absolute pressure of 33.4-16.5 kPa (9.9-4.9 in. Hg). Thereafter, the solid prepolymer was crushed and pulverized in a powder having a maximum particle size of 297 microns (100% through 50 mesh screen).

The resin powders were yellow in color, and had an average melting point of 95-105°C (203-221°F) and volatile content of 21 percent. The unmodified precursors were used to prepare foam sheets for use in flexible resilient seating applications and the FSB modified precursors were used for fabrication of thermal acoustical insulation materials.

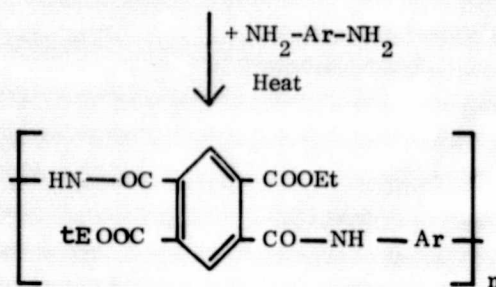
3.3.8 Reactions; Esterification, Amidization, Imidization

The reactions that occur during the resin synthesis and subsequent foaming are too complex to be described here. The general model is presented below:

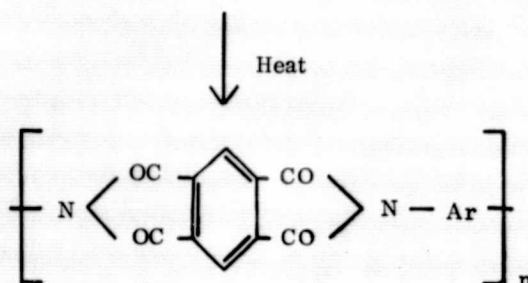
(i) Esterification:



(ii) Amidization:



(iii) Imidization:



3.4 FLEXIBLE RESILIENT POLYIMIDE FOAMS

Flexible, resilient polyimide foams were made from powder copolyimide foam precursors by the following methods; free-rise technique, multi-stage techniques, dielectric heating and microwave heating.

In the first two processes the powder resin was spread over aluminum foil (0.038 mm, 1.5 mil) laid over an aluminum plate (1.5 mm, 63 mil). Next, a powder applicator was run over the surface to produce a uniform powder coating of desired thickness. The same technique was used for the microwave and dielectric heating except that the powder was applied on Teflon sheet (3.2 mm, 0.125 inch) or other electrical insulating material since conductive surfaces are not compatible with these two heating methods. The coating thickness employed for all precursors under study in this program varied from 1.25 mm (0.05 in.) to 10 mm (0.4 in.).

The copolyimide powder precursors were then foamed in accordance with the following processes. For processes carried out by the free-rise technique, the powder was placed in a circulating air oven and held at 287.7-315°C (550-600°F) for 30 minutes. Foaming by the multi-stage technique was carried out by placing the powder into a pressure vessel contained within an oven preheated at 232.2°C (450°F) and connected to a vacuum pump via a line and regulating valve. The vessel was closed and the absolute pressure reduced to 67.1-33.4 kPa (19.9-9.9 in. Hg) while the temperature was maintained at 232.2°C for 15 to 30 minutes. The foam was then postcured at 315.5°C (600°F) for 15-30 minutes in a circulating air oven.

Foaming by microwave heating was carried out using a Gerling Moore Batch Cavity Model 4110 operating at a frequency of 2450 MHz and a power of 2.5 kW. The copolyimide powder precursors laid on Teflon sheets were preheated at 204.4°C (400°F) in a circulating air oven for 90-100 seconds and then placed

in the microwave cavity. After 3 minutes of applied microwave energy, the foam was removed and postcured at 287.7°C (550°F) for 15 to 30 minutes. Foaming by dielectric heating was carried out utilizing a Thermex Model TBGA High Frequency Generator operating at a nominal frequency of 27 MHz. The copolyimide powder was laid on a sheet of G-7 glass-silicone laminate and placed on a surface preheated to 121°C (250°F) and the high frequency field was applied. After 20-40 seconds the foam was removed and postcured at 287.7°C (550°F) for 15 to 30 minutes.

For each of the processes, the foam rise, cellular structure, resiliency, striations, density, resistance to high humidity environments and flammability characteristics were determined to screen the most promising foam precursors and foaming processes.

The Gerling Moore Batch Cavity Model 4115 for foaming the polyimide precursors by microwave techniques is shown in Figure 4.

Foaming by dielectric heating was carried out by the Votator Division of Chemetron Corporation, Louisville, Kentucky. A typical dielectric heating unit is shown in Figure 5. Typical foams obtained from thermal and multi-stage processes are shown in Figure 6.

The flammability characteristics of the foams were obtained by vertical burn test, horizontal burn test and determination of the smoke density in accordance with the NBS procedure utilizing the NBS Smoke Density Chamber (Ref. American Instrument Co., Aminco Catalog No. 4-5800, Instruction No. 941). Figures 7a, 7b, and 7c show horizontal burn tests of flexible polyimide foams after 1 minute, 5 minutes and 10 minutes exposure. The NBS Smoke Density Chamber is shown in Figure 8. The relative flammability of the foams were determined by measuring the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support combustion of the material. The test apparatus for this determination was prepared in accordance with ASTM Designation D-2863.

Humidity tests were carried out in a vapor-temperature controlled relative humidity chamber. This is a mechanical convection controlled humidity tester manufactured by Blue M Electric Company. Using this chamber, foam samples were subjected to 100 percent relative humidity test at a dry bulb temperature of 75°C (165°F) for a period of seven days. Failure was detected qualitatively by embrittlement or degradation of the foam in the early phase of the program and by loss in indentation load deflection for final characterization of the candidate materials.

Resiliency was determined by the ball rebound method according to the procedure described in ASTM Designation D-1564, Suffix B using a tester fabricated and calibrated with the same procedure.

Mechanical tests, which included tension and elongation, dry heat, tear resistance and indentation load deflection were carried out using an Instron Universal Test Machine and the tests made in accordance with ASTM Designation D-1564 which covers standard methods of testing of slab flexible urethane foams. Compression set of the foams was tested according to the same ASTM



Figure 4.

Microwave Oven Gerling Moore
Model 4110



Figure 5.

Thermex Heater, Model CP40-B
Chemetron Corp.

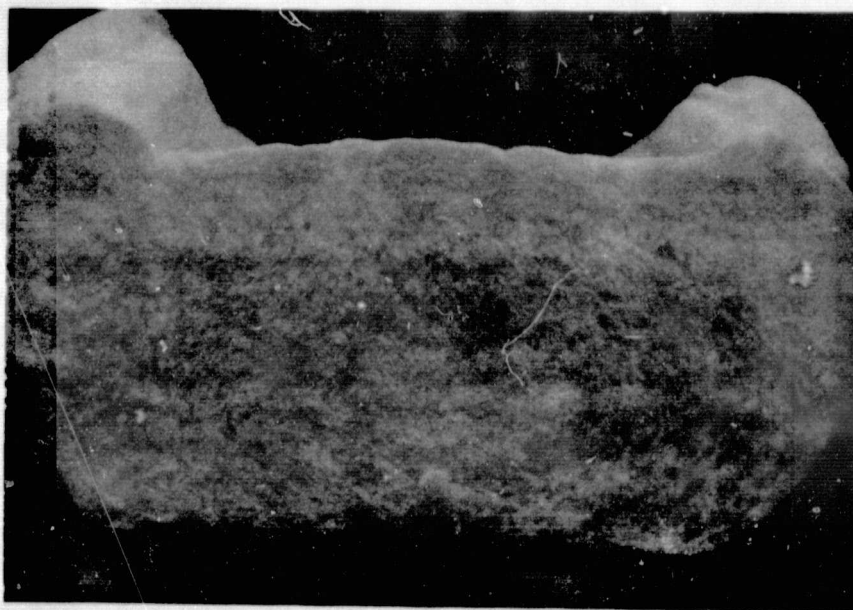


Figure 6a. Foaming by Thermal Processes (FR-160-2)

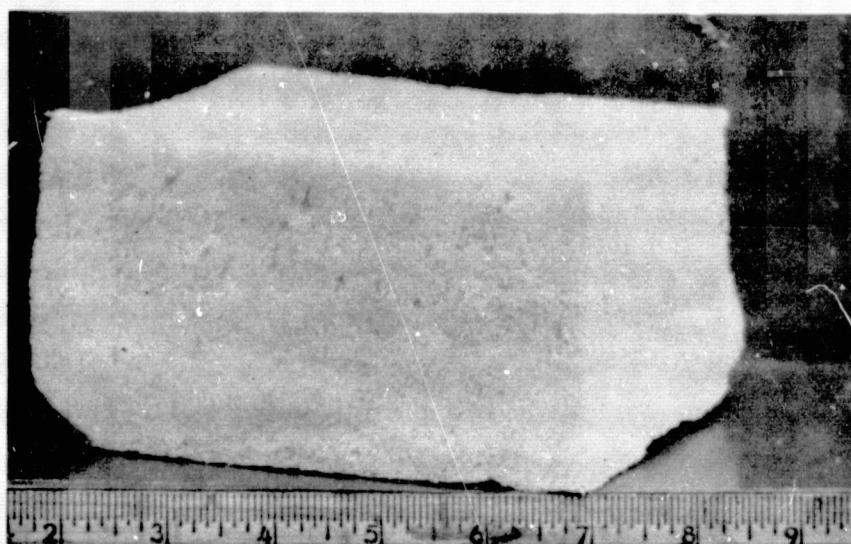


Figure 6b. Foaming by Vacuum Processes (FR-170-1)

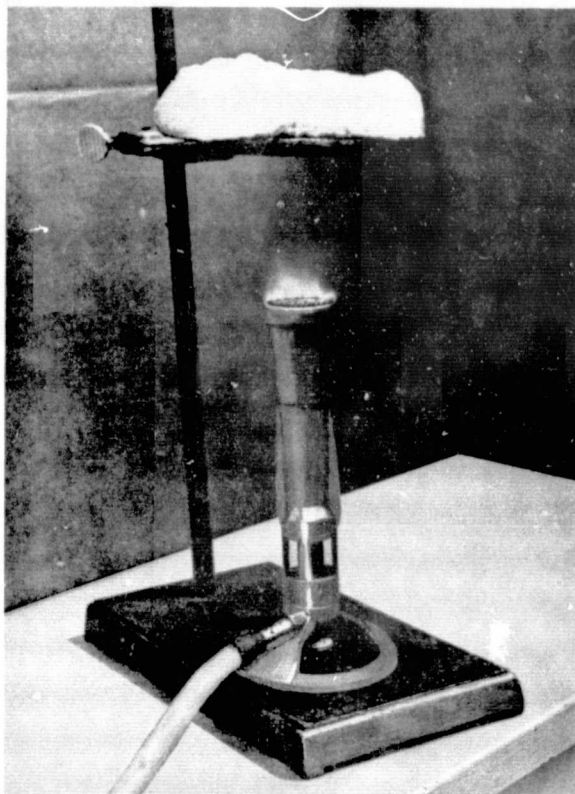


Figure 7a. Meker Burner Test - 1 Minute Exposure

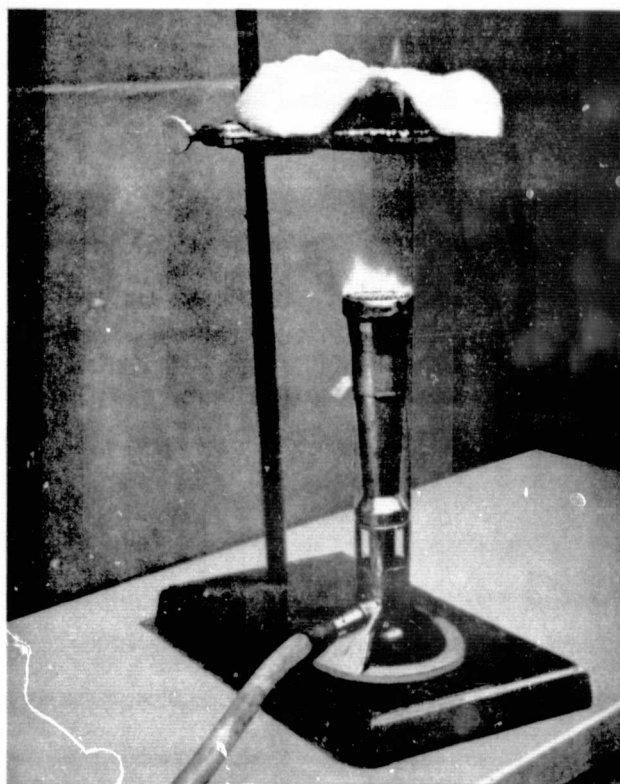


Figure 7b. Meker Burner Test - 5 Minutes Exposure

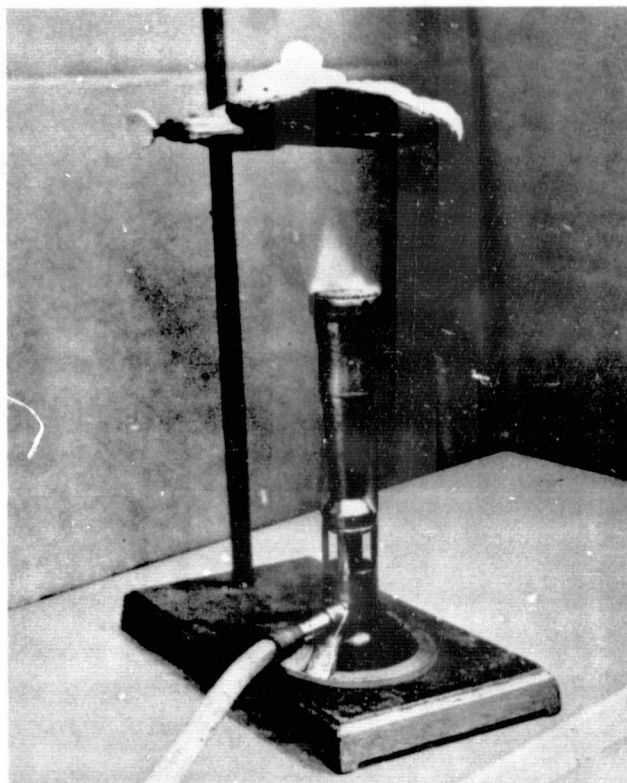


Figure 7c. Meker Burner Test - 10 Minutes Exposure

Designation D-1564 using two aluminum plates held parallel to each other by clamps and the space between the plates adjusted to the required thickness by means of spacers. The resistance of the foam to cyclic shear-loadings (fatigue test) was tested in accordance with ASTM Designation D-1564, Procedure B with the exception that examination and measurement of the foam for loss of indentation load deflection at 65 percent deflection was made at 10,000 and 20,000 cycles. The fatigue tester was constructed in accordance with the same ASTM Designation and is shown in Figure 9. Thermogravimetric analysis of the foams, determined in air, was conducted by the West Coast Technical Service, Cerritos, California. Density tests were made in accordance with ASTM Designation D-1564, Suffix W. Other tests involved visual observation of the products for cellular structure, foaming behavior and imperfections.

3.5 LAMINATE FLOOR AND WALL PANELING

The procedure for preparation of the polyimide resin precursors for use in fabrication of floor and wall panels was essentially that used in the preparation of liquid and powder polyimide precursors for use in flexible resilient foams as described in Section 3.3. The major effort of this task involved improvement of the mechanical properties of the foams through the use of a variety of methods, which included:

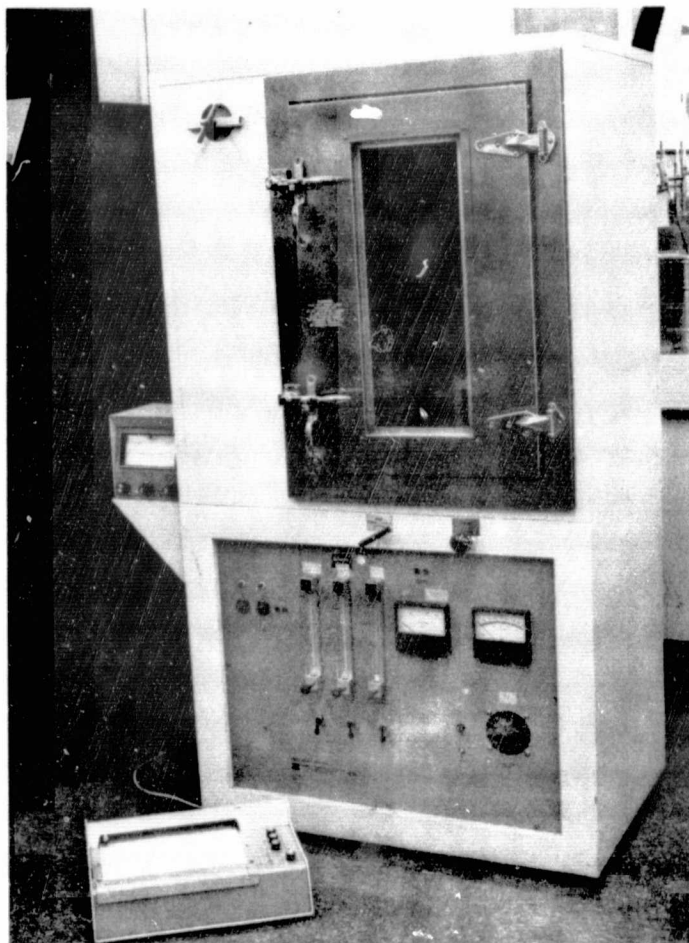


Figure 8. NBS Smoke Density Chamber

- a) reinforcing fillers
- b) addition of surface active agents or additives
- c) modification of process parameters.

Laminate floor and wall panels were obtained preferentially from the liquid resin precursors. The process consisted of compounding the liquid resin with selected fillers in a variable speed mixer for 5-20 minutes or until the fibers or fillers were thoroughly wetted. This mixture was then spread out on coated fabrics or an aluminum foil over a specified area, depending upon the final density and thickness desired, and the solvent removed by drying in a circulating air oven at 71-93°C (160-200°F). The resin composition was then foamed at a temperature of 287-315°C (550-600°F) for 15-30 minutes and compressed to the desired thickness in a platen press at 260-315°C (500-600°F) and a pressure of 34-68 kPa (5-10 psi). Figure 10 shows the three steps for preparation of rigid panels using the resin of system 160 reinforced with 1.25 cm (0.5 in.) long graphite fibers. The wet composition spread over aluminum foil (left), the foamed panel (right) and the compressed rigid panel (center) are shown.

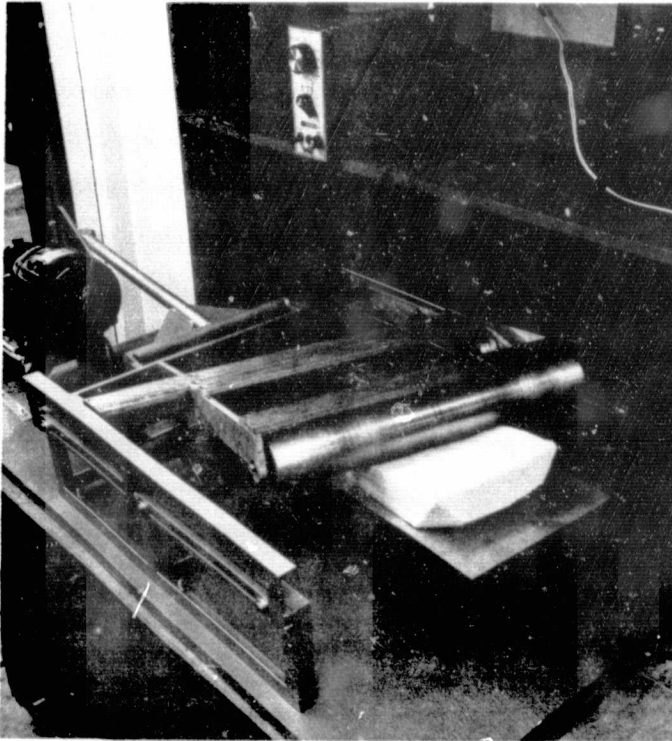


Figure 9.

**Flexible Resilient Foam -
Fatigue Tester**

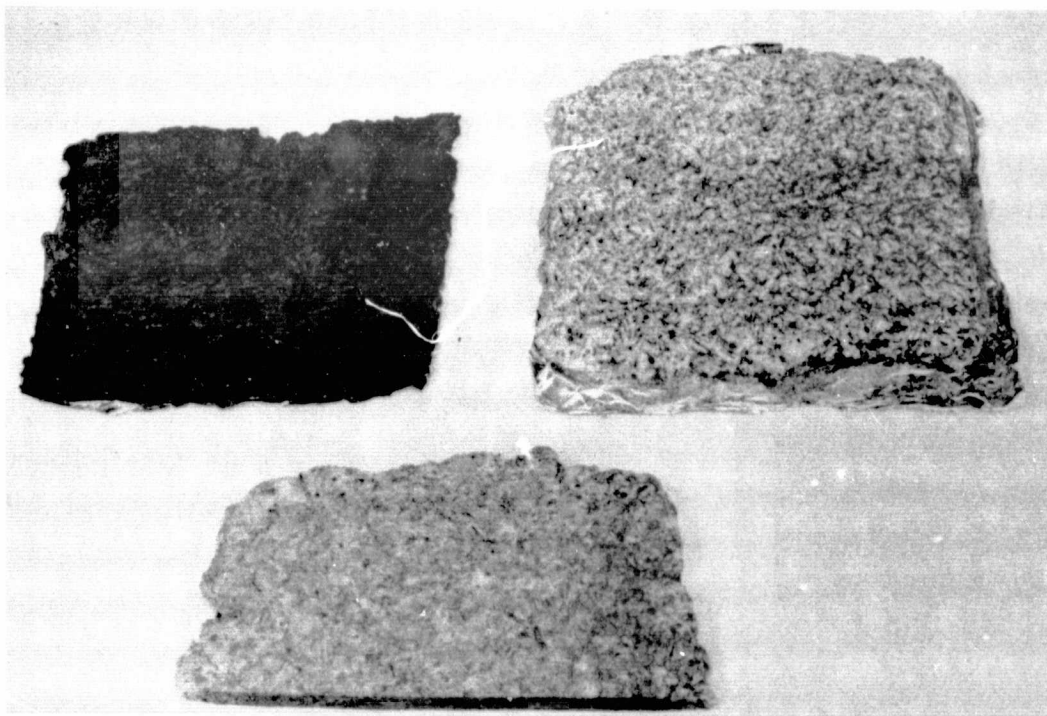


Figure 10. Preparation of Rigid Panels From Short Graphite Fibers

Rigid panels were also produced from continuous low density materials such as carbon mat. The process for fabrication of these materials was essentially that described above with the exception that the mat was first dipped in the liquid polyimide precursor followed by drying and foaming. Figure 11 shows the sequence of steps for preparation of rigid panels from mats (left) followed by foaming (center) and compression (right). Figure 12 shows a large floor panel made from carbon mat filled E-160-5 resin.

The second configuration of rigid panel was the polyimide foam filled honeycomb structure. This configuration utilizes commercially produced honeycomb sheets of either glass or Nomex paper composition. In their original condition these panels have good compressive strength, low density and are available in a variety of sizes and thicknesses. The honeycomb cells were filled with low density polyimide foam. For this application the resin precursors were used in the liquid precursor stage without the addition of surface agents or reinforcing fillers. The honeycomb panel was first dipped into the resin solution several times to fully coat the cell surface area. The panel was then dried in a vertical position to allow excess resin to collect in the bottom of the cells. Drying was carried out in a circulating air oven for a period of 14 to 16 hours at a specific temperature in the range of 82-93°C (180-200°F), depending on the resin used. The panels were then foamed at 287.7-316°C (550-600°F) for 15-30 minutes. During the heating process the resin foamed up to completely fill the cells. The panel was then surface finish with the honeycomb to provide a level plane for bonding the panel skins.

The rigid panels prepared in the early phase of this program were used to determine the effectiveness of the various fillers and resins and for screening candidates for further optimization. Initial tests included visual observation followed by determination of compressive strength, flexural strength and burning characteristics. Compression tests were carried out by a modified form of ASTM-C-365 using a test specimen size of approximately 2.5 cm x 2.5 cm (1 x 1 in.) with the thickness varying depending upon the density desired. The apparatus used was an Instron model TM-SM with a full scale load range of 500 kg and crosshead speed range of 0.05 to 10.0 cm/min. Testing was done by centering the specimen between the two compression plates and then engaging the crosshead drive. Once the recorder had shown that contact had been made, the crosshead was allowed to travel the desired distance and then it was reversed. The maximum load on the load cell as indicated by the recorder was taken to be the compressive strength of the specimen at that deflection. Each specimen was tested at several different thicknesses corresponding to different densities. After testing at one thickness, the specimens were compressed to higher density in the platen press at 260-315°C (500-600°F) and allowed to cool before retesting. The data from these tests, therefore, provided values of the compressive strength of one specimen at different densities. The average values of specimens cut from different parts of the same panel was used to construct strength density curves for that resin.

Determination of the flexural strength was carried out by a modified form of MIL-STD-401 using a test specimen size of approximately 7.5 cm x 17.5 cm.

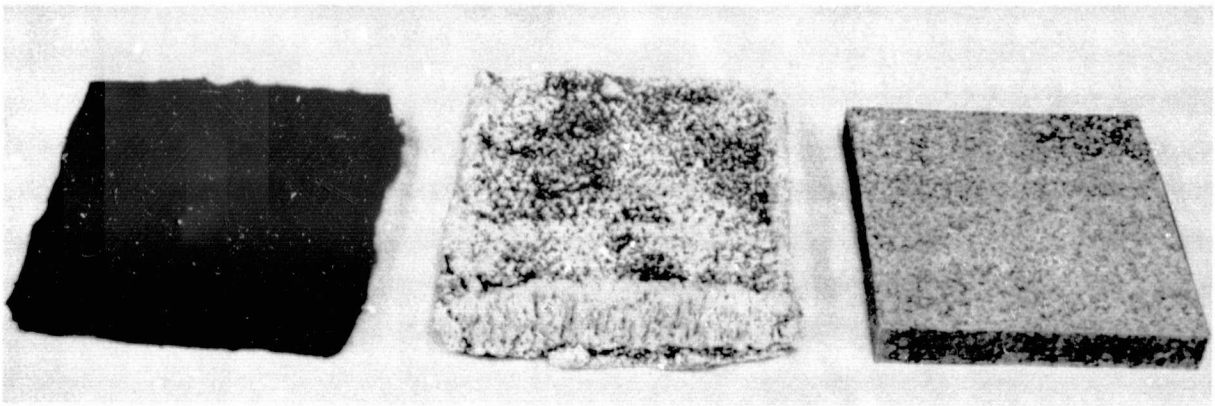


Figure 11. Preparation of Rigid Panels From Continuous Mat Materials

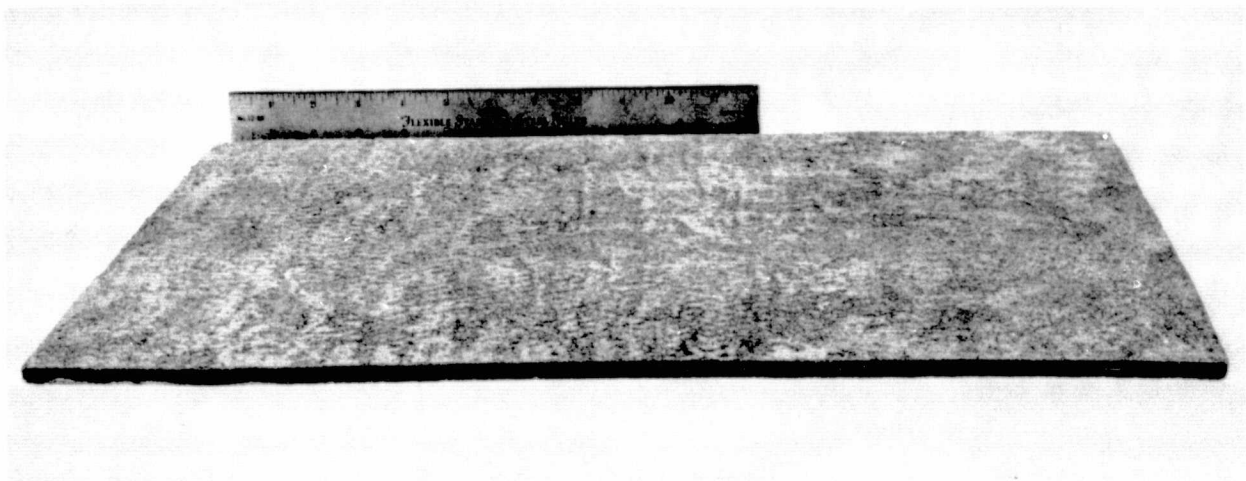


Figure 12. Carbon Mat Filled Floor Panel Resin E-160-5

The burning characteristics of the rigid panels were obtained by horizontal burn test by observing flame penetration at various time intervals for a duration of up to 10 minutes when the specimens were subjected to a Meker burner, by determination of the smoke density in accordance with the NBS procedure and by measuring the relative flammability of the panels by the use of the Oxygen Index Tester as shown in Section 3.4. Figure 13 shows a sample of rigid panel produced by foaming a carbon mat filled 160-5 resin after 10 minutes' exposure to a Meker burner having a tip flame temperature of 1260°C (2300°F).



Figure 13. Burn Test

3.6 THERMAL ACOUSTICAL INSULATION MATERIAL

Thermal acoustical insulation foams were produced from essentially the same powder copolyimide foam precursors and the same processes used for the flexible, resilient foams. After foaming, the foam rise, cellular structure, skin formation, resiliency, density, resistance to high humidity and wicking were determined for screening of candidate materials. All tests were carried out in accordance with the procedures described in Section 3.4. Wicking characteristics were obtained by the procedure described in document QR6-4501, "Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Aircraft and Spacecraft", Section 5-13, under the caption "Wicking of the Material as Received". Samples were cut from the foam material with the 6-inch length in the direction of roll and parallel to the width of the roll. Tests were carried out at room temperature and at 49°C ($120 \pm 5^{\circ}\text{F}$) for a period of 7 days. Progress of the test was recorded qualitatively by visual inspection every 24 hours with respect to penetration of water above water line and formation of precipitate. At the end of the test period, samples were inspected under microscope for any physical distortion of cellular structure submerged in water.

The acoustical absorption coefficient of the polyimide foams was measured using a Type 4002, Bruel and Kjaer Standing Wave Apparatus in conjunction with a signal generator and a sound level recorder. Figure 14 shows the test equipment.

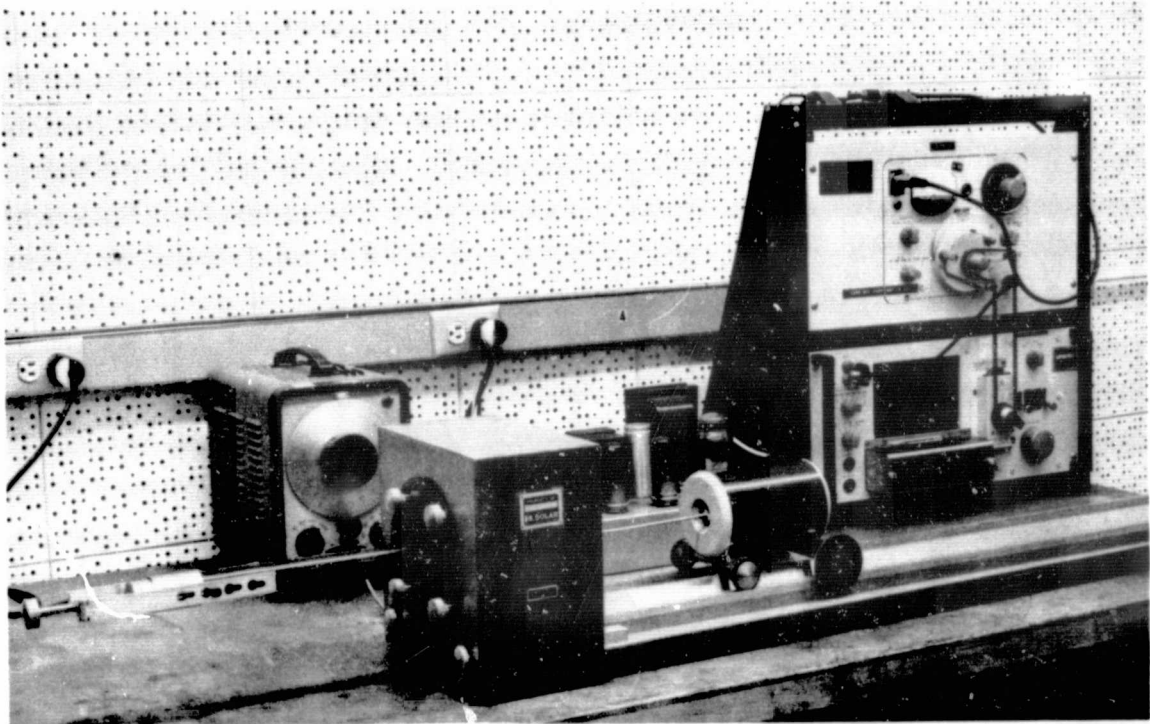


Figure 14. Bruel and Kjaer Standing Wave Apparatus Type 4002

Thermal-acoustical insulation materials were also produced by coating or foaming a polyimide resin on one surface of conventional fiberglass mat insulation material presently used in commercial aircraft. This development was undertaken to prove the feasibility of these approaches and to produce prototype samples for evaluation of the flammability characteristics using the methods described previously. The coating was applied by spray techniques using a DeVilbiss spray gun with a fluid tip D. Foaming was carried out using thermal processes as reported in Section 3.4.

3.7 HIGH STRENGTH POLYIMIDE MOLDED SHAPES

High strength polyimide molded shapes were produced by first fabricating rigid panels in accordance with the procedure described in Section 3.5, followed by compressing the panels in a electrically heated platen press. The degree of densification of the molded parts depends upon the force applied to the platens and upon the composition of the material as it relates to the reinforcement and to the type of polyimide resin used. Depending upon the force applied, the final molded parts were either completely sintered or compressed to high density porous materials. For the applications recommended in this program, process conditions which produced molded parts possessing properties characteristic for the materials compressed to just before resin sintering starts to occur, favored high impact strength. Impact is an important requirement for these materials. These characteristics were

achieved by compressing the rigid panels in an electrically heated platen press at a temperature of 287.7°C to 315.5°C (550-600°F) and a pressure of 3.4×10^2 to 34×10^2 kPa (50-500 psi) for 15-30 minutes. The platens were cooled to below 260°C (500°F) and the part removed. The tooling used for compressing the rigid panels to molded flat sheets consisted of two 6061 type aluminum plates, while a mold fabricated from low carbon steel was used for more exact configurations. Complex geometrical configurations have not been attempted with this molding process. The high density molded parts were then used for screening tests to select optimum compositions and process conditions and for final characterization of the candidate material.

Initial screening tests involved little more than visual observation of the product followed by determination of the most critical property. The Izod impact strength of the material was selected as the most critical property since similar polyimide materials have shown to be deficient in this respect.

The Izod test specimens were prepared and tested in accordance with ASTM D-758-58 and D-265-73 using the test apparatus shown in Figure 15. Figure 16 shows untested specimens cut from molded sheets and the characteristic brittle failure of the same specimens tested for impact strength.

Determination of the tensile strength and elongation was done in accordance with ASTM Designation D-638 using an Instron Universal Test Machine. Figure 17 shows tested and untested tensile specimens machined from a molded sheet. The value of the heat deflection temperature of the material was obtained in accordance with ASTM Designation D-638. The hardness of the material was measured using a Rockwell Hardness Tester Model 3R shown in Figure 18 with a 1.25 cm (0.5 in.) diameter ball indenter in accordance with ASTM Designation D-785. The chemical, physical and flammability tests were made in accordance with the procedures and apparatus described in Sections 3.4 and 3.5.

3.8 FLEXIBLE POLYIMIDE COATED FABRICS

These materials were produced by coating commercially available open weave or knitted fabrics with a polyimide resin to upgrade the fire hardening properties of the fabrics. The coating was applied by spraying techniques at a coating thickness of 2-30 mils using a DeVilbiss spray gun with a fluid tip D. The fabric was then dried at 93°C (200°F) for 5-15 minutes to remove the excess solvent and stored for subsequent final curing. Curing was done in a circulating air oven at a temperature of from 204°C (400°F) to 315°C (600°F) for 10-60 minutes. Initial tests of the coated fabric involved little more than visual observation for coating uniformity followed by tape adhesion tests to measure the degree of adhesion to the substrate and by flexibility tests to screen out candidate materials. Figure 19 shows samples of coated fabrics.

The tape adhesion test was carried out by the procedure described in ASTM Designation D-3002-71. The test consisted of applying a piece of cellulosic tape (3M & Co. No. 610 or equivalent) on the fabric and pressing firmly in

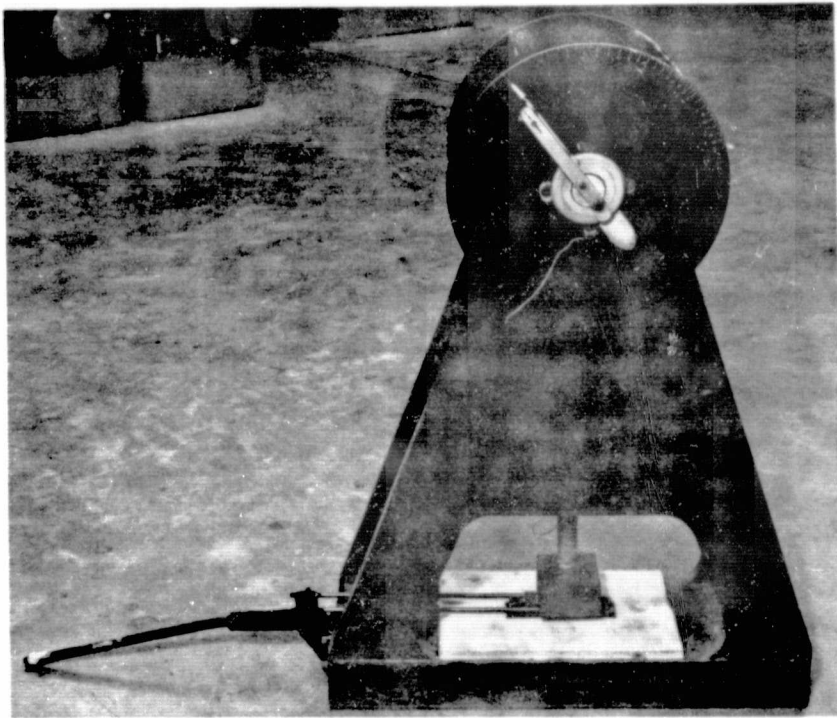


Figure 15. Izod Tester

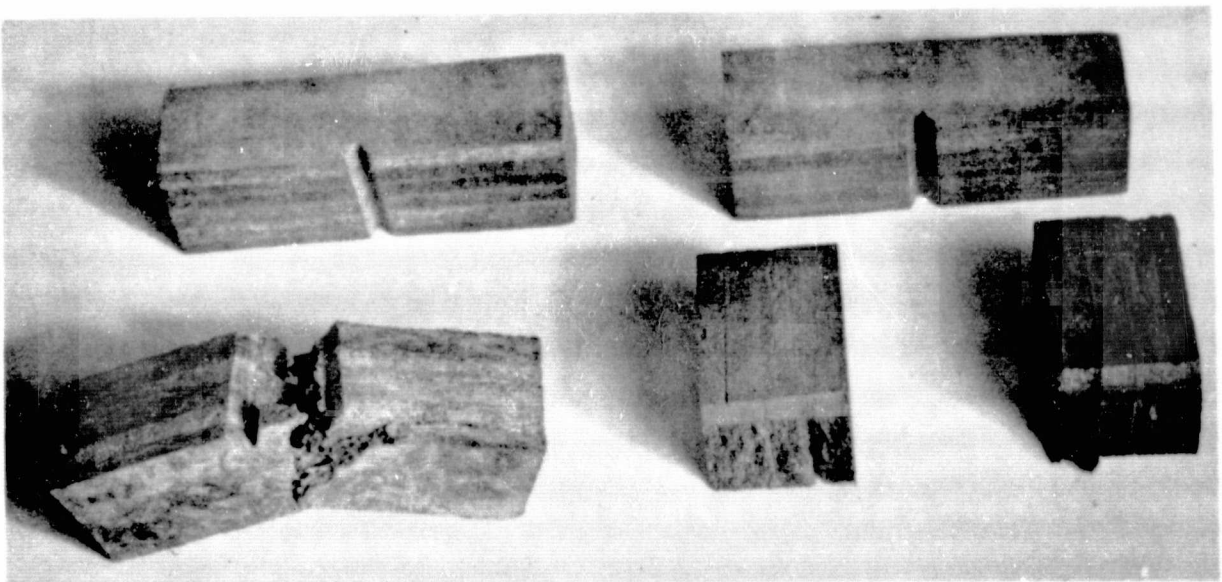


Figure 16. Izod Test Specimen



Figure 17. Tensile Specimens; Molded Glass Filled 170-2 Compositions

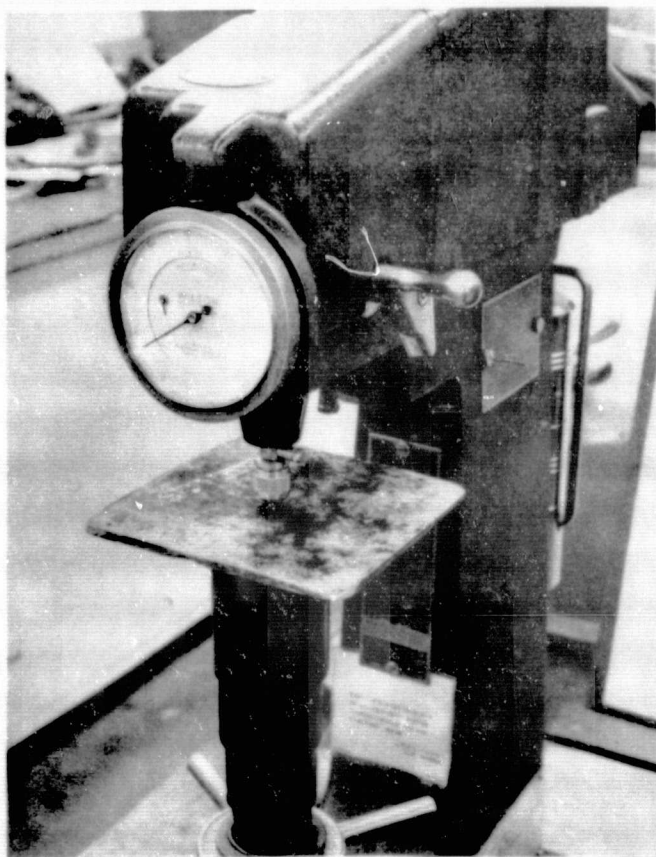


Figure 18.

**Rockwell Hardness Tester.
Molded Test Sample**

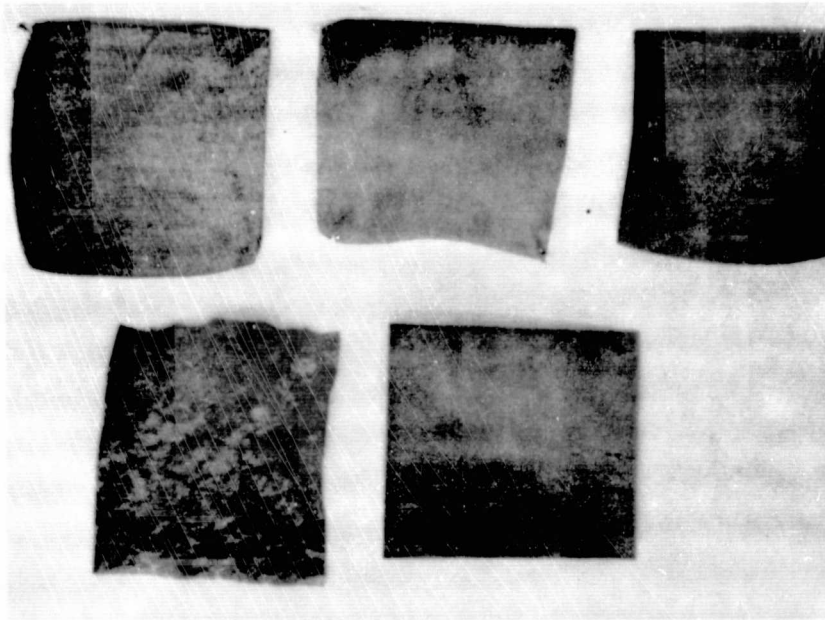


Figure 19. Polyimide Coated Fabrics. Top (left to right) Asbestos, 120 Style Glass, 180 Style Glass. Bottom (left to right) 0.5 mm (2 mil) Nomex; 2.5 mm (10 mil) Nomex

place with a hand roller. One end of the tape was lifted to a 45 degree angle and removed rapidly maintaining the same angle. The coating removed was measured and reported as a percentage of the total. The flexibility of the coating was measured by bending the fabric on a mandrel at an angle of 90 and 180 degrees followed by observation for any sign of coating failure.

After selection of the candidates, the final materials were evaluated for abrasion resistance, blocking and stiffness in accordance with the procedure described in Federal Specifications CCC-T-191b and for bursting strength and flex-crack resistance in accordance with ASTM D-751-68 and D-2176-69 respectively. The tests reported above were carried out by the United States Testing Company, Inc. in Los Angeles, CA. Flammability, physical and chemical characteristics were evaluated in accordance with the methods described in Sections 3.4 and 3.5.

4

EXPERIMENTAL RESULTS

This section covers the work dealing with the experimental data and advanced modifications of all products studied in this program and is organized in accordance with the following schedule: flexible resilient polyimide foams (Section 4.1) followed in the order by laminate floor and wall paneling (Section 4.2) thermal acoustical insulation (Section 4.3), high strength polyimide molded shapes (Section 4.4) and polyimide coated fabrics (Section 4.5).

4.1 FLEXIBLE RESILIENT POLYIMIDE FOAMS

This section describes the work relevant to the optimization of polyimide foams, possessing a high degree of resiliency and flexibility, for use in aircraft seating applications. This effort starts with the synthesis of advanced polyimide precursors (Section 4.1.1) followed in the order by foaming studies (Section 4.1.2), scale-up processes for fabrication of large specimens (Section 4.1.3), characterization and selection of candidate materials (Section 4.1.4) and final fabrication of samples for submittal to NASA-LBJ Space Center (Section 4.1.5).

4.1.1 Advanced Polyimide Synthesis

This task starts with the work pertinent to re-evaluation of the hydrolytic stability of the most promising flexible resilient polyimide foams developed under NAS9-14718, NASA-LBJ Space Center, and to establish meaningful structure to property relationships.

A total of 33 copolyimide foam precursors were synthesized in Task I of NASA-LBJ Space Center, contract NAS9-14718. An additional six copolyimide foam precursors were synthesized subsequent to that effort. Out of these 39 precursors, seven were selected and the foams re-evaluated for hydrolytic stability. None of the foams contained surfactants or other additives. The foam selected for humidity tests, their compositions, and pertinent physical properties are reported in Table IV. The humidity test was carried out at 73.9°C (165°F) and 100 percent relative humidity for a period of seven days by the test method described previously.

To better correlate the test data, the foams produced from the 4,4'DADPS system shown in Table IV, have been listed in order of decreasing 2,6DAP

Table IV
Re-Evaluation of Polyimide Foams for Hydrolytic Stability
at 73.9 C and 100% RH

Foam Resin Number	Composition	Molecular Ratio	Density kg/m ³	Aging Time, Hours		
				48 Hours	120 Hours	168 Hours
31	BTDA:2,6DAP:4,4'DADPS	1:0.95:0.05	16.0	Brittle	Friable	Disintegrated
25	BTDA:2,6DAP:4,4'DADPS	1:0.85:0.15	27.0	Brittle	Friable	Disintegrated
15	BTDA:2,6DAP:4,4'DADPS	1:0.75:0.25	29.0	Brittle	Friable	Disintegrated
1	BTDA:2,6DAP:4,4'DADPS	1:0.5:0.5	29.5	Little or no Change	Brittle	Disintegrated
16	BTDA:2,6DAP:4,4'DADPS	1:0.25:0.75	39.0	Little or no Change	Brittle	Brittle
35	BTDA:2,6DAP:4,4'DADPS	1:0.15:0.85	47.0	Little or no Change	Slightly Brittle	Brittle
36	BTDA:2,6DAP:4,4'DADPS	1:0.05:0.05	58.5	Little or no Change	Slightly Brittle	Brittle
17	BTDA:2,6DAP:MDA	1:0.2:0.8	58.0	Little or no Change	Little or no Change	Little or no Change
19	BTDA:2,6DAP:mPDA	1:0.3:0.7	58.5	Little or no Change	Slightly Brittle	Brittle
29	BTDA:2,6DAP:TDA	1:0.85:0.15	43.7	Little or no Change	Brittle	Disintegrated

molar ratio. Resin No. 31 (0.95 M 2,6DAP), resin No. 25 (0.85 M 2,6DAP) and resin No. 15 (0.75 M 2,6DAP) degraded after 48 hours of exposure. Resin No. 1 (0.5 M 2,6DAP) and resin No. 16 (0.25 M 2,6DAP) began to show signs of degradation after 120 hours of test. Resin No. 35 (0.15 M 2,6DAP) and resin No. 36 (0.05 M 2,6DAP) began to loose resiliency after 168 hours of exposure.

Figure 20 shows the typical failure of the foams produced from Resin No. 31; total foam collapse occurred after 72 hours exposure followed by total degradation after 168 hours. Although incipient embrittlement was noticeable, the foams produced from resin No. 35, made at the lowest ratio of 2,6DAP, maintained cellular integrity without sign of degradation or collapse after 7 days of exposure. The molar ratio of the heterocyclic diamine (2,6DAP) to aromatic diamine (4,4'DADPS) has thus proved to have a marked influence on the hydrolytic stability of polyimide foams. Low molar ratio of 2,6DAP has shown to improve the hydrolytic stability but to adversely affect the flexibility and resiliency of the foams, however, this deficiency has been overcome as it will be discussed later. Further improvements have been achieved by using diamines with higher primary amine dissociation constants as shown by the results obtained with resin No. 17 and 19. This latter approach was investigated in greater depth in the section dealing with advanced polyimide synthesis of selected systems reported below. Finally very significant improvements were achieved by more efficient foaming methods as it will be discussed in Section 4.1.2.

On the basis of the data obtained in the re-evaluation of the hydrolytic stability of the foams, three resin systems were selected for further study; these are:

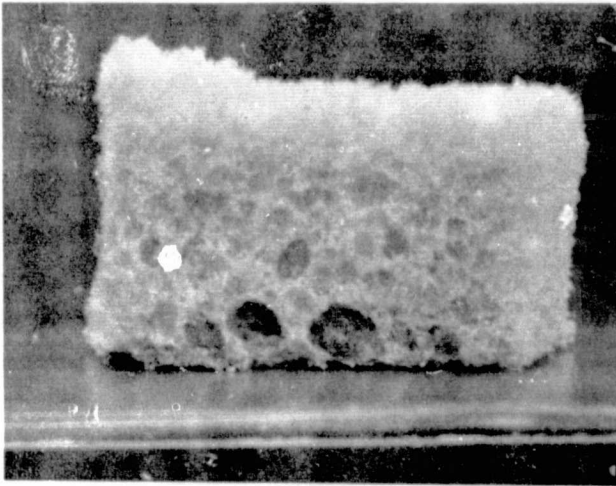


Figure 20a.

Before the Humidity Test

Figure 20b.

After 72 Hours in Humidity Test

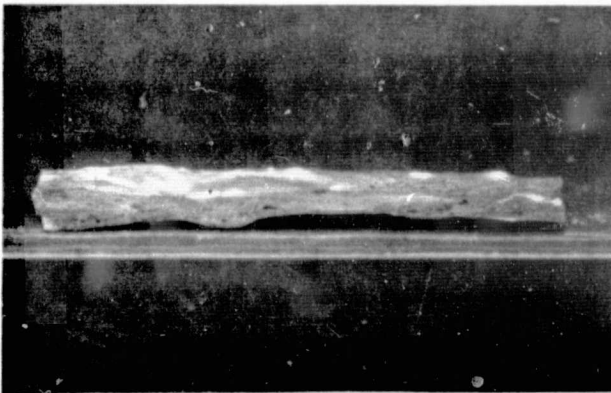
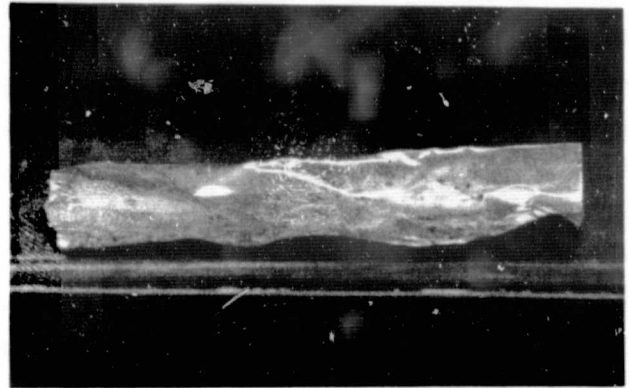


Figure 20c.

After 7 Days in Humidity Test

- (i) BTDA:2,6DAP:4,4'DADPS (160 system, resin 16 of NAS9-14718)
- (ii) BTDA:2,6DAP:MDA (170 system, resin 17 of NAS9-14718)
- (iii) BTDA:2,6DAP:mPDA (190 system, resin 19 of NAS9-14718)

The major objective of this study involved the modification of the selected systems to define the parameters which influenced cellular structure, density, flexibility, resiliency, and most of all resistance of the foams to deterioration in high humidity environments. This study was pursued through four separate but complimentary schemes which involved modification of the polymer structure by chemical alteration of the copolyimide system, evaluation of excess reactants, re-evaluation of esterifying agents, and modification of the polyimide precursors with selected additives, surface active agents, and foaming agents.

In the first phase dealing with chemical alteration of the polymeric structure, a total of 26 polyimide foam precursors were synthesized belonging to 160, 170 and 190 series. Summary of important experimental data derived from this study is given in Table V.

After selection of the most promising compositions a total of 76 additional, advanced polyimide foam precursors were synthesized to evaluate surface active agents and their effects on the cellular structure. Summary of important experimental data derived from this study is given in Table VI. The study of foaming agents is presented in Table VII.

A discussion of the results derived from the study of the chemical alteration of the three compositional systems is presented succinctly in the sequence: (1) system BTDA:2,6DAP:4,4'DADPS, (2) system BTDA:2,6DAP:MDA and (3) system BTDA:2,6DAP:mPDA. The discussion of advanced synthesis of selected polyimide candidates is then continued in the sequence: (4) evaluation of excess reactants, (5) evaluation of esterifying agents, (6) evaluation of surface active agents, foaming agents, and additives and (7) selection of optimum candidates.

(1) The System BTDA:2,6DAP:4,4'DADPS

This system was the subject of extensive study by Solar in earlier work in polyimide technology and was reported to NASA-LBJ Space Center in document NAS9-14718 (Ref. 1). At the conclusion of that program it was found that foams produced from this system were deficient in two major areas, fatigue strength and hydrolytic stability. In the present program new compositions have been synthesized to overcome these deficiencies, starting with studies of chemical alteration to enhance the hydrolytic stability. The polyimide foam precursors and foam characteristics for the three compositional systems under study have been shown in Table V. The results show that the limit of the molar concentration of 2,6DAP necessary to achieve flexibility and resiliency varied for each of the systems under study. For the 160 series, this limit is 0.2 moles of 2,6DAP. This indicates that flexible and

Table V

Advanced Polyimide Foam Precursors and Foam Characteristics
Effect of Mole Ratio, Excess Reactants, and Esterifying Agent

Foam Resin Number	Composition	Molecular Ratio	BTDA Half Ester	M.P., °C	Volatile %	Excess (2.5%)	Type of Foam
160-0	BTDA:2,6DAP:4-4'DADPS	1:0.25:0.75	Ethyl	128.5-135	17.55	BTDA Diamines	Flexible, resilient, fine cellular structure
160-1	BTDA:2,6DAP:4-4'DADPS	1:0.35:0.65	Ethyl	120-127	18.44		Flexible, resilient, fine cellular structure
160-2	BTDA:2,6DAP:4-4'DADPS	1:0.40:0.60	Ethyl	127-130	18.62		Flexible, resilient, fine cellular structure
160-3	BTDA:2,6DAP:4-4'DADPS	1:0.30:0.70	Ethyl	123-130	17.87		Flexible, resilient, fine cellular structure
160-4	BTDA:2,6DAP:4-4'DADPS	1:0.15:0.85	Ethyl	119-126	17.33		Semi flexible, resilient, good structure
160-5	BTDA:2,6DAP:4-4'DADPS	1:0.20:0.80	Ethyl	120-124	17.65		Flexible, resilient, fine cellular structure
160-6	BTDA:2,6DAP:4-4'DADPS	1:0.15:0.85	Methyl	110-119	16.72		Semiflexible, semiresilient
160-7	BTDA:2,6DAP:4-4'DADPS	1:0.20:0.80	Methyl	108.5-115	17.23		Flexible, resilient, fair structure
160-8	BTDA:2,6DAP:4-4'DADPS	1:0.20:0.80	Ethyl	120-125	18.90		Flexible, resilient, fair structure
160-9	BTDA:2,6DAP:4-4'DADPS	1:0.20:0.80	Ethyl	115-120	19.30		Brittle structure
170-0	BTDA:2,6DAP:MDA	1:0.50:0.50	Ethyl	105-116.5	20.04	Diamines BTDA	Flexible, resilient, fine cellular structure
170-1	BTDA:2,6DAP:MDA	1:0.40:0.60	Ethyl	110-119	19.71		Marginally flexible and resilient, good structure
170-2	BTDA:2,6DAP:MDA	1:0.30:0.70	Ethyl	106-116	18.99		Semiflexible, semiresilient, good structure
170-3	BTDA:2,6DAP:MDA	1:0.20:0.80	Ethyl	108.5-115	17.89		Rigid foam, good structure
170-14	BTDA:2,6DAP:MDA	1:0.40:0.60	Methyl	90-95	17.65		Low rise, semi-rigid foam
170-15	BTDA:2,6DAP:MDA	1:0.40:0.60	n-Propyl	123-130	18.65		Flexible, resilient, good structure
170-6-R	BTDA:2,6DAP:MDA	1:0.40:0.60	Ethyl	100-110	18.81		Flexible, resilient, good structure
170-7-R	BTDA:2,6DAP:MDA	1:0.40:0.60	Ethyl	100-110	18.34		Flexible, resilient, good structure
190-0	BTDA:2,6DAP:mPDA	1:0.50:0.50	Ethyl	115.5-125.5	21.40	BTDA Diamines	Flexible, resilient, fine structure
190-1	BTDA:2,6DAP:mPDA	1:0.40:0.60	Ethyl	118.5-127.5	21.60		Moderately flexible, and resilient, fair structure
190-2	BTDA:2,6DAP:mPDA	1:0.60:0.40	Ethyl	107.5-121	21.64		Flexible, resilient, fine cellular structure
190-3	BTDA:2,6DAP:mPDA	1:0.30:0.70	Ethyl	112.5-122	21.10		Marginally flexible and resilient, fair structure
190-4	BTDA:2,6DAP:mPDA	1:0.30:0.70	Methyl	92-102	19.83		Slightly flexible and resilient, brittle structure
190-5	BTDA:2,6DAP:mPDA	1:0.60:0.40	Methyl	92-102	19.85		Poorly flexible and resilient, poor structure
190-6	BTDA:2,6DAP:mPDA	1:0.50:0.50	Ethyl	108-112	21.35		Marginally resilient, poor cellular structure
190-7	BTDA:2,6DAP:mPDA	1:0.50:0.50	Ethyl	110-114	21.78		Flexible, resilient, fair structure

Table VI

Properties of Flexible Foams With Surface Active Agents

Resin	Additive	Additive Concentration (%)	Precursor MP, °C	Precursor Volatile (%)	Foam Density		Resiliency	Foam Characteristics
					lbs/ft ³	Kg/m ³		
160-0	-	-	109-113	17.2	1.37	21.95	85	Flexible, resilient, fine cellular structure
160-0-11	L-5420	0.2	102-107	17.5	1.31	20.99	88	Flexible, resilient, fine homogeneous cellular structure
160-0-12	L-5340	0.2	110-116	16.4	1.31	20.99	70	Flexible, good cellular structure
160-0-13	L-5410	0.2	101-106	18.9	1.31	20.99	70	Marginally flexible, brittle cellular structure
160-0-15	L-530	0.2	109-112	18.1	0.87	13.94	70	Flexible, homogeneous, fine cellular structure
160-0-16	L-520	0.2	109-112	18.4	0.69	11.05	80	Flexible, homogeneous, fine cellular structure
160-0-17	L-550	0.2	111-116	16.7	2.37	37.97	65	Marginally flexible, brittle cellular structure
160-0-18	DC 190	0.2	104-112	16.0	1.56	24.99	60	Flexible, homogeneous, cellular structure, dark in color
160-0-19	DC 193	0.2	102-110	17.6	1.75	28.03	<50	Brittle cellular structure
160-0-21	DC 196	0.2	114-121	17.5	1.43	22.91	<50	Flexible, fair cellular structure
160-0-22	Victamide 511	0.2	107-116	17.1	1.31	20.99	70	Brittle cellular structure
160-0-23	FSB	0.2	101-110	18.06	0.56	8.97	<50	Flexible, very homogeneous, fine cellular structure
160-0-24	FSC	0.2	102-112	17.6	0.75	12.01	<50	Flexible, very homogeneous, fine cellular structure
160-0-27	FC 431	0.2	112-115	17.3				Poor cellular structure, brittle foam
160-0-28	FC 430	0.2	108-115	17.5				Poor cellular structure, brittle foam
170-1-38	L-5420	0.2	105-109	18.4	1.42	22.75	80	Flexible, resilient, fair cellular structure
170-1-39	FSB	0.2	99-108	20.2	0.80	12.82	60	Flexible, resilient, very homogeneous, fine cellular structure
170-1-40	FSC	0.2	97-102	20.3	0.63	10.09	70	Flexible, resilient, good cellular structure
170-1-41	L-520	0.2	99-105	18.5	1.10	17.62	70	Slightly brittle, large cellular structure
170-1-42	L-530	0.2	94-102	19.0	2.07	33.16	<50	Very brittle structure
170-1-43	FSB	0.1	95-103	18.9	0.83	13.29	75	Flexible, resilient, good cellular structure
170-1-45	FSB	0.5	96-104	19.5	0.72	11.53	<50	Flexible, marginally resilient, very fine homogeneous cellular structure; shrinks on cooling
170-1-46	FSB	1	97-102	19.0	1.50	24.03	50	Flexible, poorly resilient, fine cellular structure; shrinks on cooling
170-1-47	FSB	0.05	102-112	18.1	1.30	20.83	75	Flexible, fair homogeneous cellular structure
170-1-48	FSC	0.05	94-111	18.0	1.03	16.50	75	Flexible, good homogeneous cellular structure

Table VII
Study of Foaming Agents and Additives

Foam No.	Precursor Series	Additive	Additive Concentration (%)	Density		Resiliency	Foam Characteristics
				lbs/ft ³	Kg/m ³		
F-786	170	Celogen C.T.	1	1.23	19.70	50	Poor cellular structure
F-787	170	Celogen C.B.	1	1.20	19.22	55	Poor cellular structure
F-788	170	Celogen HT 550	1	1.15	18.42	50	Poor cellular structure
F-785	170	L-170	0.4	3.10	49.66	<50	Cross-linking occurs, rigid foam

resilient foams are obtained over a wider range of concentration of heterocyclic diamine and that the property of the foams of this system are less dependent to compositional changes than that of the other two systems.

This characteristic has also been evidenced by the effect of compositional changes on the density of the foams. The density profile for the three compositional systems prepared at the reactant ratios reported in Table V is shown in Figure 21. The density of the foams of the 160 series are least dependent on the molecular composition as demonstrated by the low slope of the curve.

Although flexibility and resiliency have been achieved at low 2,6DAP ratio, the foams of the 160 series are degraded when exposed to high humidity environments. Table VIII presents a summary of the tests made with foams produced from the resins of the 160 series after exposure to 73.9°C (165°F) and 100% RH for a period of seven days. The data reported is significant since it supports the findings derived from the preliminary re-evaluation of foams where the relationship between molar ratio of 2,6DAP and hydrolytic resistance of the foams was first found. This relationship is demonstrated again by the increasing stability to humid environments of foams produced at decreasing molar ratio of 2,6DAP.

In conclusion, as shown in Table V, the mechanical and physical properties of foams made from the three compositional systems have been found to be closely related to the 2,6DAP ratio. Low ratio produces foams with fine cellular

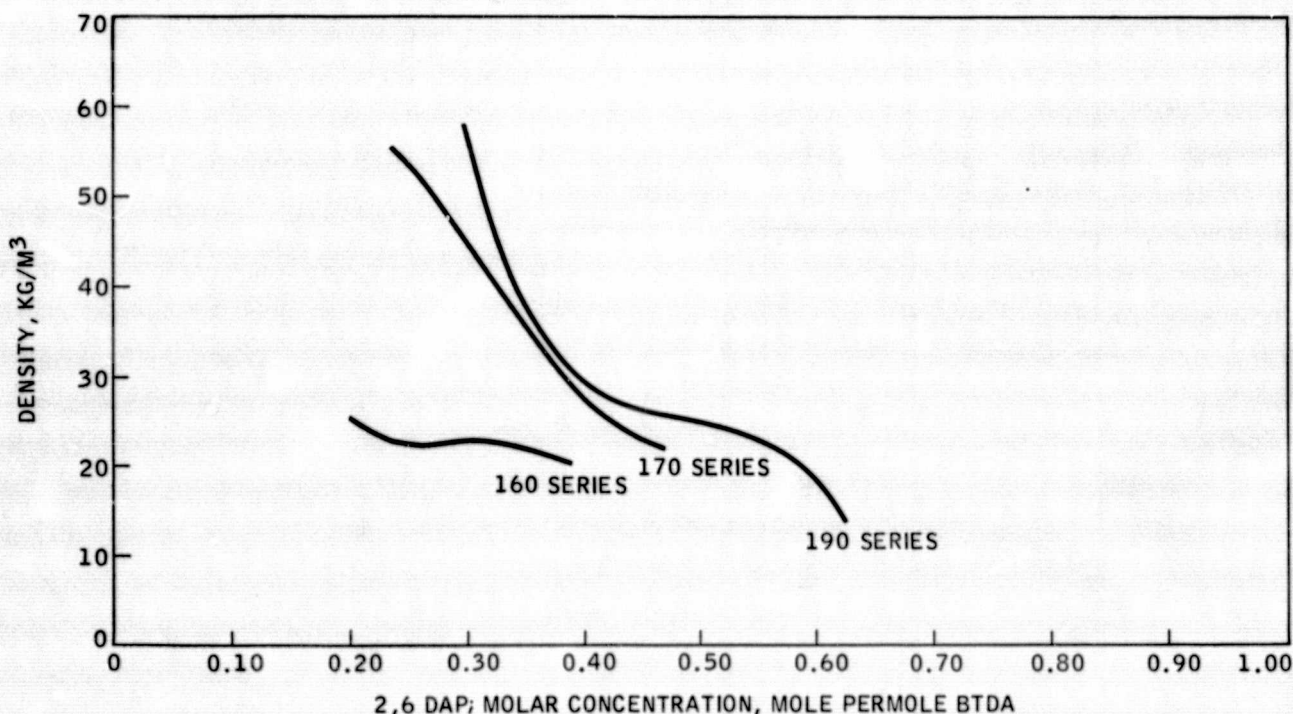


Figure 21. Density Profile of Flexible Polyimide Foams

Table VIII
160 Series; Hydrolytic Stability of Polyimide Foams
at 73.9 C and 100% RH

Foam Resin Number	Composition BTDA:2,6DAP:4,4'DADPS	Condition After 48 Hours	Condition After 120 Hours	Condition After 168 Hours
160-2	1:0.4:0.6	Little or no Change	Friable Foam	Friable Powder
160-1	1:0.35:0.65	Little or no Change	Friable Foam	Friable Powder
160-3	1:0.3:0.7	Little or no Change	Friable Foam	Friable Powder
160-0	1:0.25:0.75	Little or no Change	Friable Foam	Friable Powder
160-5	1:0.2:0.8	Little or no Change	Slightly Brittle	Brittle Foam
160-4	1:0.15:0.95	Little or no change	Slightly Brittle	Brittle Foam

structure, low foam rise, high density, improved hydrolytic stability but higher rigidity and flexibility. The fire resistance of the foams did not show to be affected by changes in composition. Foams from the 160 series have produced thermoplastic deformation and shrinkage when impinged with direct flames; this behavior was less noticeable with foams produced from the other two systems. At the conclusion of this study dealing with chemical alteration, the foam precursors of the 160 series have shown to possess deficiencies for use in applications requiring resiliency, flexibility and hydrolytic resistance, however, the ease of processing and the properties exhibited by the foams makes these resins desirable candidates for other products under study, specifically rigid panels and molded shapes.

(2) The System BTDA:2,6DAP:MDA

Most of the work performed on this system has been under this contractual effort. Summary of the humidity tests made with foams produced from this system is shown in Table IX. A breakthrough was achieved in the evaluation of the resins of 170 series when it was found that these foams possessed good resistance to high humidity environments at medium concentration of 2,6DAP in addition to good flexibility and resiliency. Foams prepared from precursor 170-1 (1:0.4:0.6) were only slightly affected at the end of the humidity test period (7 days) as indicated in Table VIII. Figure 22(a) shows this foam before and at the end of the humidity test [Fig. 22(b)]. No collapse or shrinking of the foam occurred during the test as it was shown to occur with foams of the 160 series (Fig. 20) at the same 2,6DAP ratio.

During this phase of the program, foams prepared from polyimide precursors made at a 2,6DAP molar ratio below 0.4 were at best marginal in resiliency and flexibility. Figure 23 shows foams belonging to the 170 series at

Table IX
170 Series; Hydrolytic Stability of Polyimide Foams
at 73.9 C and 100% RH

Foam Resin Number	Composition BTDA:2,6DAP:MDA	Condition After 48 Hours	Condition After 120 Hours	Condition After 168 Hours
170-0	1:0.5:0.5	Little or no Change	Slightly Brittle	Friable Foams
170-1	1:0.4:0.6	Little or no Change	Little or no Change	Slightly Brittle
170-2	1:0.3:0.7	Little or no Change	Little or no Change	Very Slightly Brittle
170-3	1:0.2:0.8	Little or no Change	Little or no Change	Little or no Change

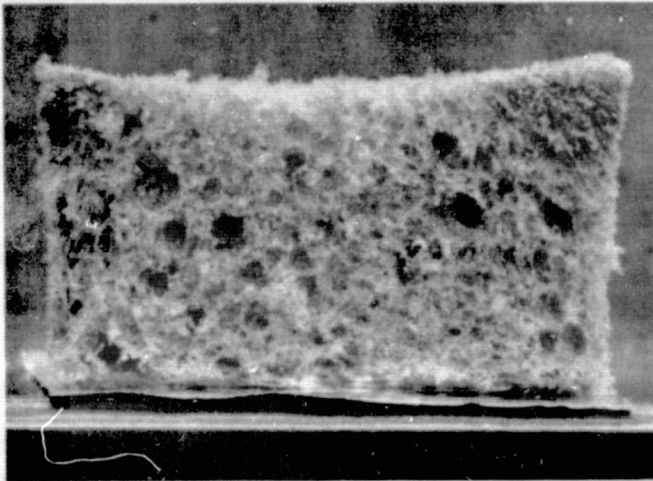
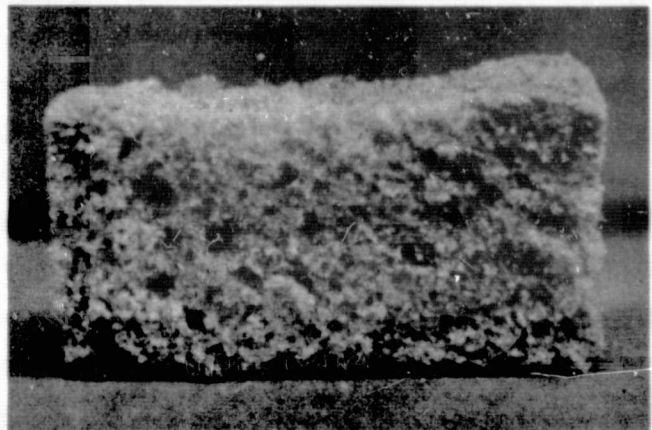


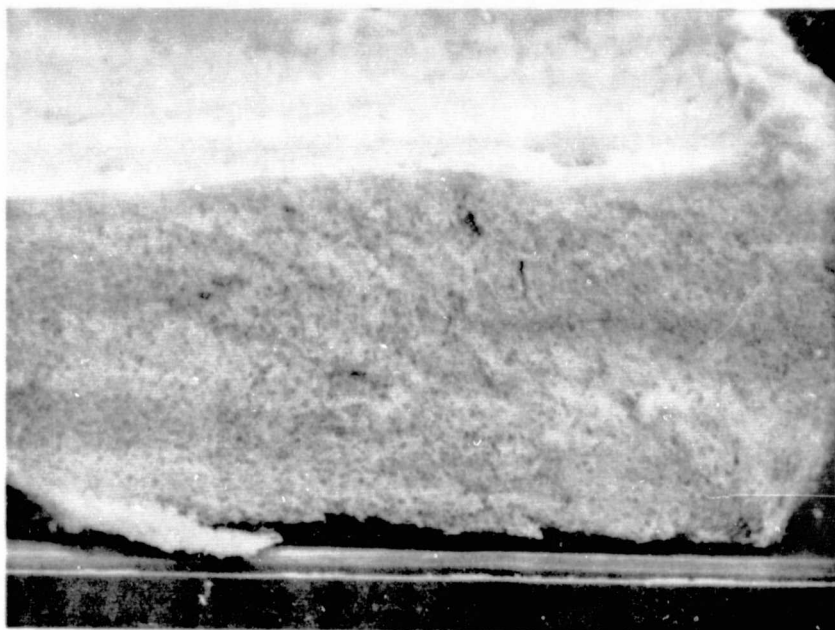
Figure 22a.

Polyimide Foam. FR 170-1 -
Untested

Figure 22b.

Polyimide Foam FR 170-1 After 7
Days at 73.9 C (165 F) and 100%
RH



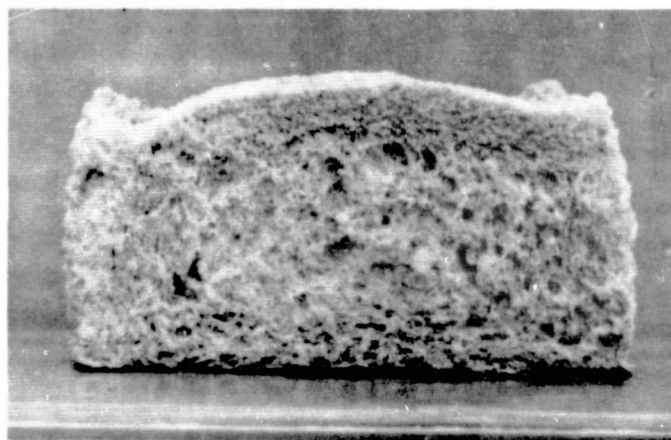


A

Foam Resin No. 170-0
0.5M 2,6DAP; 0.5M MDA

B

Foam Resin No. 170-1
0.4M 2,6DAP; 0.6M MDA



C

Foam Resin No. 170-2
0.3M 2,6DAP; 0.7M MDA

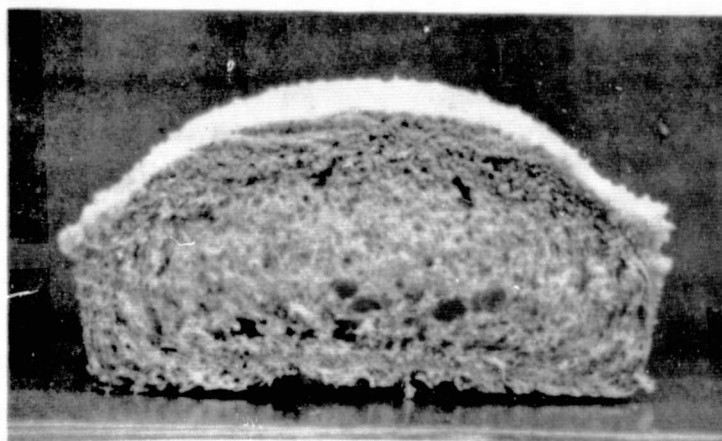


Figure 23. Polyimide Foams, 2,6DAP:MDA System. Effect of Heterocyclic Diamine Concentration on Foam Rise and Cellular Structure.

various ratio of 2,6DAP. Figure 33(a) presents a foam specimen made from 170-0 precursor (0.5 moles 2,6DAP). The foams possessed a very fine cellular structure, which generally contributes to high resiliency (70% by ball rebound) and flexibility. The cellular structure of foams produced from 170-1 precursor (0.4 moles 2,6DAP) [Fig. 33(b)] shows irregularities but the foam possesses an acceptable degree of resiliency (55% by ball rebound) and flexibility, however the foams made from precursor 170-2 (0.3 moles, 2,6DAP) [Fig. 23(c)] exhibited a high degree of surface densification and were considerably less flexible and resilient (30% by ball rebound). Although the range of molecular ratio of the heterocyclic diamine has been found to be more critical with the 170 system than with any other system evaluated to date, studies dealing with optimization of process parameters, which will be reported in Section 4.1.2, have shown that a combination of improved reaction conditions and addition of selected surface active agents will result in polyimide precursors which, at a 2,6DAP ratio as low as 0.2, produced flexible, resilient foams.

The flexibility of the polyimide foams belonging to the three compositional systems has been found to be dependent not only upon molar ratio of the heterocyclic diamines, but also upon the type of aromatic diamines used in the preparation of the precursors as it is shown in Figure 24. At the same molar ratio of 2,6DAP, foams produced from precursors made with 4,4' diamino diphenyl sulfone possessed the highest degree of flexibility [Fig. 24(c)], followed by those made with methylene dianiline [Fig. 24b] while meta phenylene diamine [Fig. 24a] contributed to foams exhibiting marginal rigidity and stiffness characteristics.

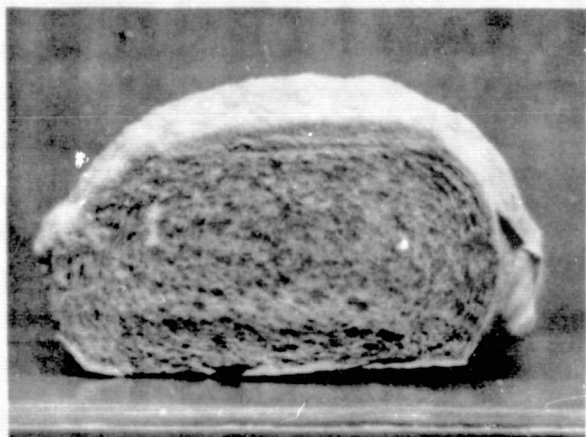
(3) The System BTDA:2,6DAP:mPDA

Surprisingly, foams produced from this system have shown to possess poorer hydrolytic stability than foams from the other two systems although meta phenylene diamine has been known to yield strong imide linkages. Summary of the humidity tests made with foams produced from this system is shown in Table X.

Due to unexpectedly poor hydrolytic stability, this system has been eliminated from the list of candidates for use in flexible and resilient seating applications.

(4) Evaluation of Excess Reactants

The task dealing with evaluation of the effects of tetraacid or diamine excess was undertaken with the objective to improve the hydrolytic stability and cellular structure of polyimide foams and to alleviate the problem of striations known to be the principal factors in fatigue failure of polyimide foams. The significance of this work is the deliberate control of molecular weight of the polyamic acid precursor to facilitate the development of homogeneous cellular structure during foaming.

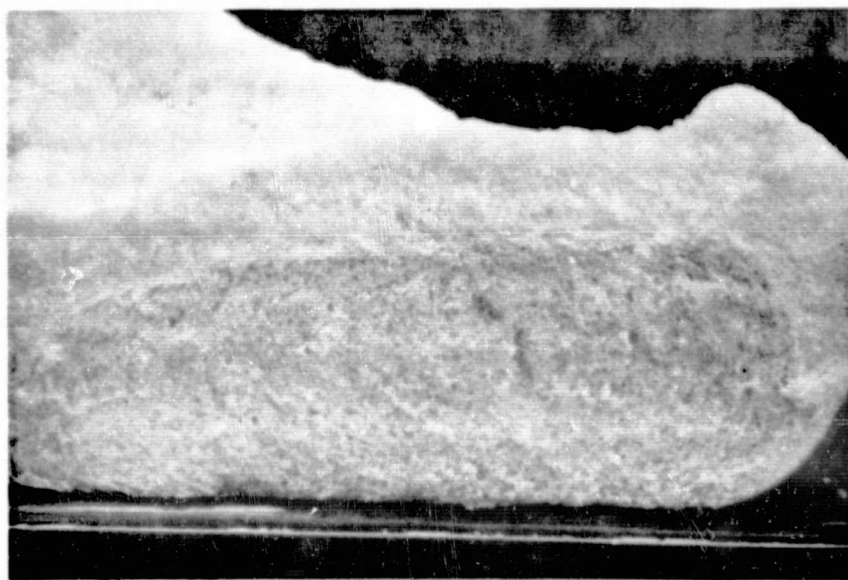
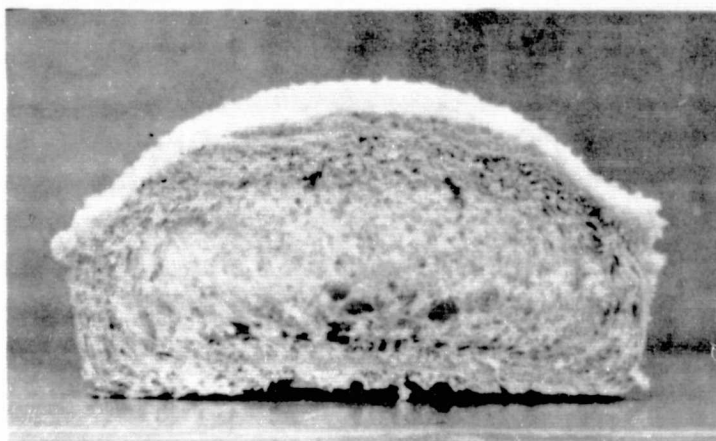


A

Foam Resin No. 190-3
0.3M 2,6DAP; 0.7M mPDA

B

Foam Resin No. 170-2
0.3M 2,6DAP; 0.7M MDA



C

Foam Resin No. 160-3
0.3M 2,6DAP; 0.7M
4,4'DADPS

Figure 24. Polyimide Foams. Effect of Aromatic Diamine on Foam Rise, Cellular Structure and Rigidity

Table X
190 Series; Hydrolytic Stability of Polyimide Foams
at 73.9 C and 100% RH

Foam Resin Number	Composition BTDA:2,6DAP:mPDA	Condition After 48 Hours	Condition After 120 Hours	Condition After 168 Hours
190-2	1:0.6:0.4	Slightly Brittle	Friable Powder	Friable Powder
190-0	1:0.5:0.5	Slightly Brittle	Brittle	Friable Powder
190-1	1:0.4:0.6	Little or no Change	Slightly Brittle	Friable Powder
190-3	1:0.3:0.7	Little or no Change	Slightly Brittle	Friable Powder

Table V, shown previously, reports the characteristics of foams prepared with 2.5 percent excess of the principal reactants for all compositional systems. Considerable effort has been devoted on this subject, since it was postulated that an excess reactant would produce crosslinking and improve the hydrolytic stability of the foams, however, humidity tests have shown no effect on properties. In view of these findings, all efforts on this subject were abandoned.

(5) Evaluation of Esterifying Agents

The principal objective of this task dealt with the evaluation of the esterifying agents used in the synthesis of the diesters of benzophenone tetracarboxylic acid to determine their effect on foam properties with major consideration on hydrolytic stability and cellular structure. Extensive studies of esterifying agents for the diaminodiphenyl sulfone system were reported in document NAS9-14718 (Ref. 1) and proved that significant changes of the foaming behavior occurred. These changes affected the foam rise, cellular structure, flexibility and resiliency.

In the present program, various compositions of the E-170-1 system were prepared using three different esterifying agents, methanol, ethanol, and propanol. The cellular structure of foams produced from the methyl esters was significantly more brittle confirming previous data, but ethyl and propyl esters produced flexible resilient foams. Figure 25 shows samples of foams produced from resin E-170-1 using the three esterifying agents; from left to right are foams made with precursors prepared from propanol, ethanol and methanol, showing the different rise and cellular structure. These foams were tested for hydrolytic resistance, but no detectable differences were found among the candidates to warrant continuation of this work.

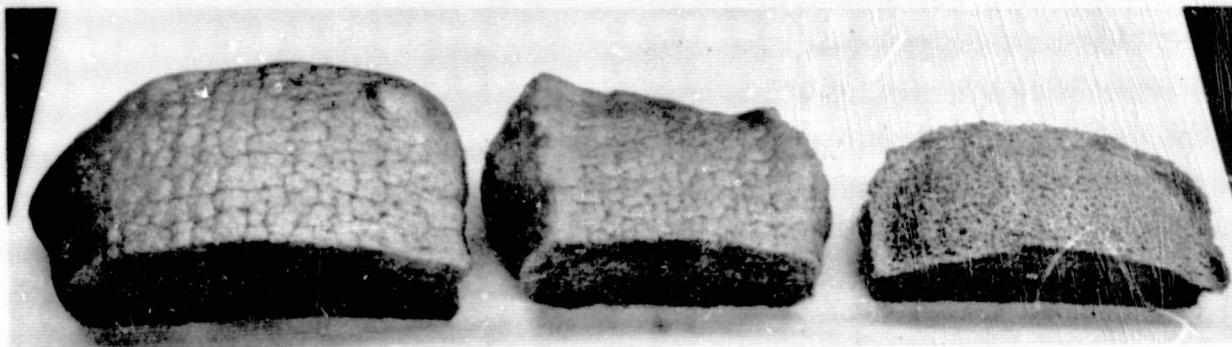


Figure 25. Esterifying Agents, Effect on Foam Properties (FR 170-1)

This investigation proved that propyl alcohol can be used in the preparation of precursors of the 170 series. This represents an economical advantage over the present ethanol system and a second choice for a raw material.

(6) Evaluation of Surface Active Agents, Foaming Agents and Additives

(i) Surface Active Agents - During the amidization and imidization reactions dealcoholation and dehydration takes place with formation of a large number of gas bubbles. Surface active agents help improve bubble stability and produce cellular structures with larger number and lower average size cells.

A total of 14 different surface active agents were selected for the study. These included silicone surfactants, fluoro surfactants and one cationic surfactant. The list of surfactants studied, their concentration based on polyimide solids, and the characteristics of the foam for the two selected compositional systems 160 and 170 are reported in Table VI.

This study indicates that FSB and FSC, two fluorosurfactants, give best results with both 160 and 170 series. The other surfactants were either incompatible or produced no significant contributions. The best surfactant, namely FSB, was also evaluated at various concentrations to obtain best balance of physical properties. The characteristics of these foams are reported in Table VI. The density profile of foams prepared from precursor modified with FSB is shown in Figure 26, where surfactant concentration is plotted against foam density. The curve indicates that increasing concentration of FSB produces a decrease of the density of the polyimide foams. This is true for concentrations up to 0.5 percent. Above this level, the density increase, again caused by a finer cellular structure which at higher surfactant concentration will collapse. Below 0.5 percent concentration, FSB produced the most significant contribution to cellular structure than any other surfactant studied to date.

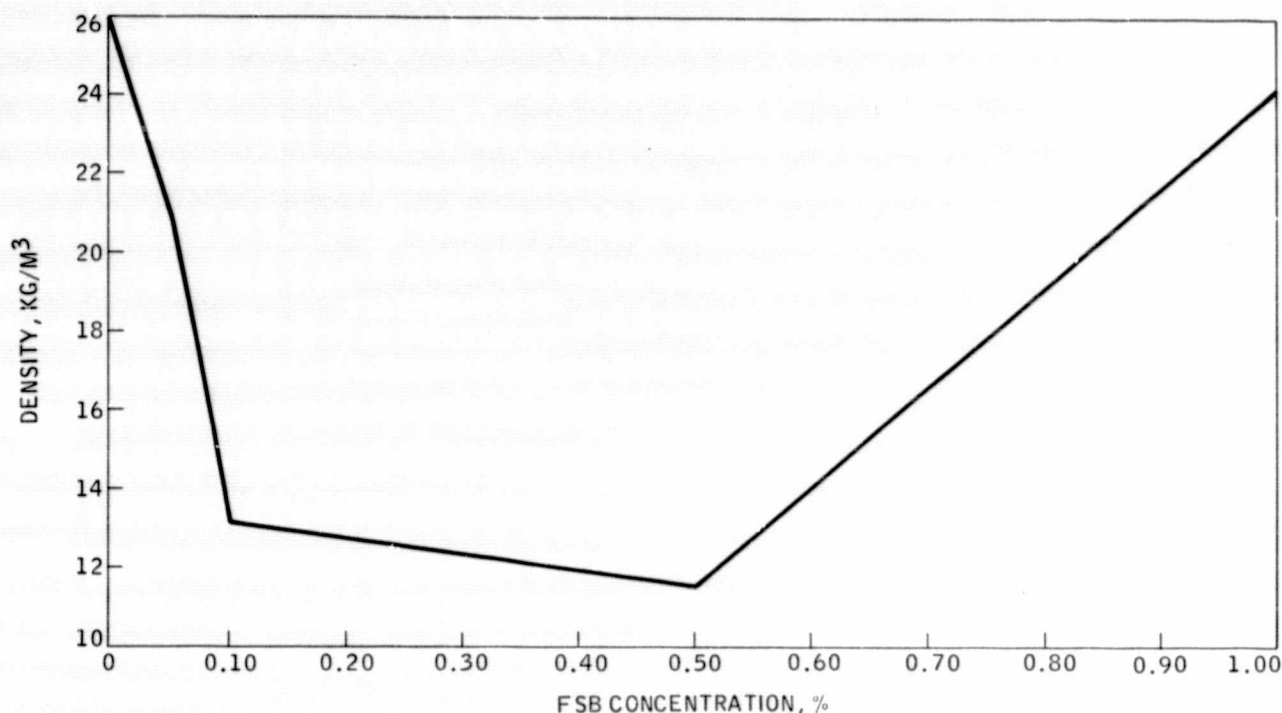


Figure 26. FSB Surfactant; Effect of Concentration on Density of Flexible Resilient Foams (FR-170-1)

The surface active agents did not have any effect on the hydrolytic stability of the foams, however, foams modified with FSB have produced more uniform test data than foams made without surfactant. This is presumed to be a result of better and more uniform cellular structures.

(ii) Foaming Agents - Foaming agents, often referred to as blowing agents, are solid, liquid, or gaseous substances which alone, or in combination with other substances, produce a cellular structure in a plastic composition. The foaming agents studied in this task belong to the category of chemical agents which produce nitrogen gas under the influence of heat and are listed in Table VII along with the characteristics of foams.

The foaming agents studied produced brittle and irregularly large cellular structure with discoloration of final product. It is believed that the secondary amino group present in these foaming agents reacts with the polyamic acid, thus interfering with the cyclization reaction and the foaming mechanism. These results did not warrant continuation of this task.

(iii) Additives - The additives investigated under this study were L-170 and L-169, which are fluorocarbon products manufactured by Imperial Chemical Corporation. Foams modified with these additives lose their flexibility and resiliency and produce foams with high density and rigidity characteristics.

Figure 27 shows the density profile of foams produced from precursors modified with L-170 at various L-170 concentrations. A rapid rise in foam density occurred up to a concentration of 0.6 percent L-170 but beyond this concentration the density remained practically constant. It appears that up to concentration of 0.6 percent, considerable crosslinking occurs, thus the foam loses flexibility. Beyond 0.6 percent, the contribution of L-170 to crosslinking is doubtful and merely serves as inert filler. These foams possessed suitable properties for use in wall and ceiling panels. Additional work is contemplated on optimization of these compositions in future work.

(7) Selection of Candidates

The selection of candidate foam precursors for further optimization and screening in later phases of this program has been carried out according to plan. In this context, properties given the most consideration in the early plan of the program were hydrolytic stability, resiliency, density, and homogeneity of cellular structure.

The 190 system, made from meta phenylene diamine, was eliminated due to inferior hydrolytic stability. Methyl alcohol was also eliminated as a candidate for the preparation of the foam precursors. Surfactants proved to be beneficial in modification of the foam precursors of the 160 and 170 series. Foaming agents and additives gave brittle and rigid foams and were

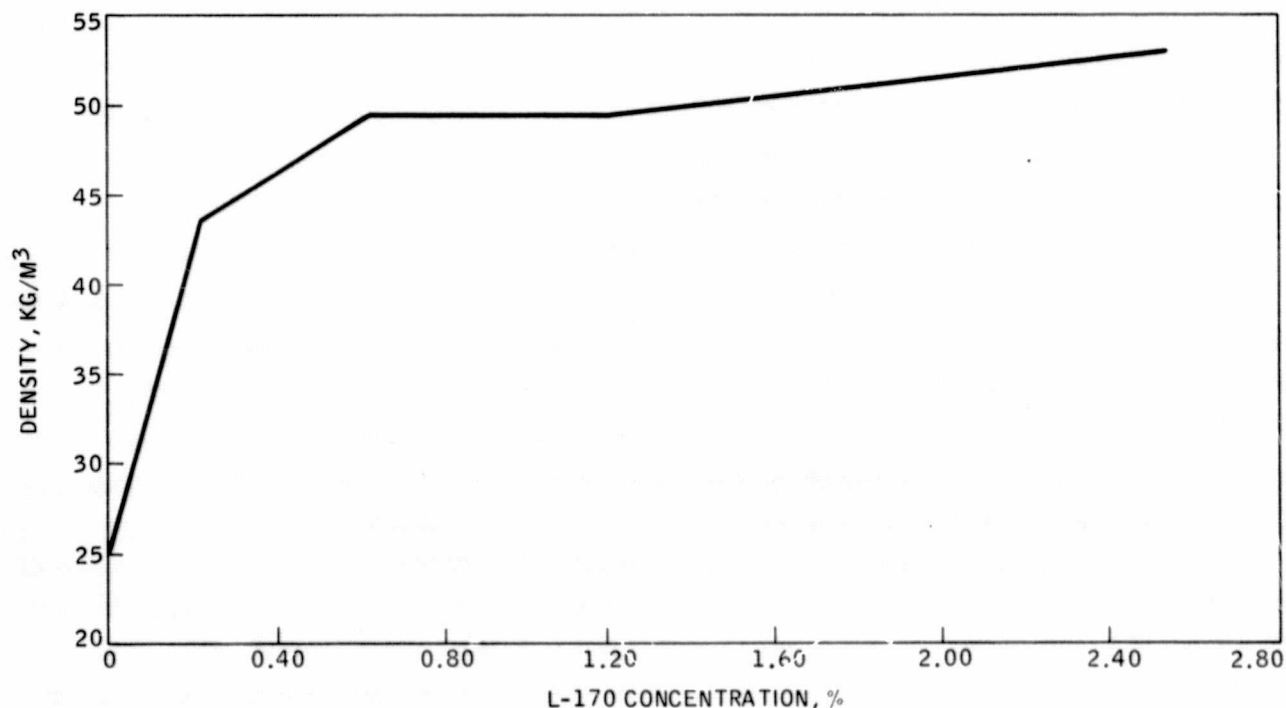


Figure 27. L-170 Additives; Effect of Concentration on Foam Density (FR 170-1)

not further considered for use in resilient foams. The study of excess reactants indicated desirability of using excess diamines for preparation of foam precursors belonging to the 170 series but additional data did not substantiate the results. On the basis of the discussion and data presented in the previous sections, the resins selected are summarized in Table XI along with compositions, reaction conditions, and recommended modification.

Table XI
Selection of Candidates

Serial No.	Foam Resin No.	Composition	Molecular Ratio	BTDA Half Ester	Surfactant	Concentration (%)	Condensation Reaction Temperature	B-Staging °C	Vacuum Heating °C
1	160-0	BTDA:2,6DAP:4-4'DADPS	1:0.25:0.75	Ethyl	FSB	0.05-0.10	Reflux	82.2	76.7
2	160-0	BTDA:2,6DAP:4-4'DADPS	1:0.25:0.75	Ethyl	-	-	Reflux	82.2	76.7
3	170-1	BTDA:2,6DAP:MDA	1:0.40:0.60	Ethyl	FSB	0.2-0.3	65-70	76.7	65.5
4	170-2	BTDA:2,6DAP:MDA	1:0.30:0.70	Ethyl	FSB	0.2-0.3	65-70	76.7	65.5
5	170-1	BTDA:2,6DAP:MDA	1:0.4:0.6	Ethyl	-	-	65-70	76.7	65.5

4.1.2 Foaming Studies

This paragraph is divided into two parts. The first part (1) outlines the studies pertinent to the optimization of processing parameters to produce the polyimide precursors, the second part is a study of new foaming methods (2). The major emphasis of this task is to investigate new heating methods capable of providing more uniform heat transfer through the rising mass and produce foams with more homogeneous cellular structure.

(1) Optimization of Process Parameters

In this study a series of experiments were conducted to investigate the influence of reaction conditions on the cellular structure, flexibility, resiliency and density of the foams in order to select an optimum process before initiation of the study dealing with new foaming methods. The parameters studied were:

- i. Condensation Reaction Temperature
- ii. B-Staging Temperature
- iii. Vacuum Heating

These are the three most critical steps in the synthesis of the polyimide precursors. These investigations were carried out with resin 170-1; this resin was selected because it produced flexible resilient foams with better resistance to high humidity than any other resin studied to date.

i. Condensation Reaction Temperature

The reactions to produce the liquid procurors are two. The first reaction involves the synthesis of the diester of benzophenone tetracarboxylic acid, which is carried out for all resins at the reflux temperature of ethyl alcohol. The second and most important reaction is that involving the condensation of the diamines with the half ester.

Three sets of different temperature conditions were selected for the condensation reaction. These conditions were:

55-60°C	(131-140°F)
65-70°C	(149-158°F)
81°C (reflux)	(178°F)

for period of times of from 5 to 60 minutes.

After the condensation reaction the resins were processed according to the standard procedure which involved B-staging in a circulating air oven at 76.5°C (170°F) followed by final heating at 65.5°C (150°F) under reduced pressure to produce the powder polyimide precursors. Table XII shows the effect of condensation temperature on the characteristics of the polyimide precursors and respective foams. On the basis of these results a temperature of 60-70°C was selected and the study of the following process parameters carried out as reported below.

ii. B-Staging Temperature

The B-staging process involves the adjustment of the volatile content of the polyimide precursors at conditions which prevent pre-polymerization reactions. At the completion of the B-staging process the resin is still essentially monomeric, a requirement for producing flexible, resilient foams.

The liquid polyimide precursors prepared at the reaction temperature of 60-70°C (140-158°F) were then B-staged in a circulating air oven at four different temperature conditions for 16 hours. These conditions were:

65.5°C	(150°F)
71.1°C	(160°F)
76.7°C	(170°F)
82.2°C	(180°F)

The precursors were then analyzed for volatile content and processed further to evaluate their foaming behavior. The volatile content of the precursors has shown to be a critical material property and to affect the foam rise and cellular structure. Figure 28 shows the effect of B-staging temperature on

Table XII
Effect of Reaction Temperature on FR-170-1

Reaction Temperature °C	Prepolymer		Foam			
	M.P., °C	Vol. %	Density lbs/ft ³	Kg/m ³	Resiliency	Cellular Structure
55-60	108-114	18.7	1.06	16.9	85	Homogeneous
65-70	110-119	18.1	1.22	19.5	85	Very homogeneous
81 (reflux)	107-115	17.4	1.62	25.9	85	Irregular

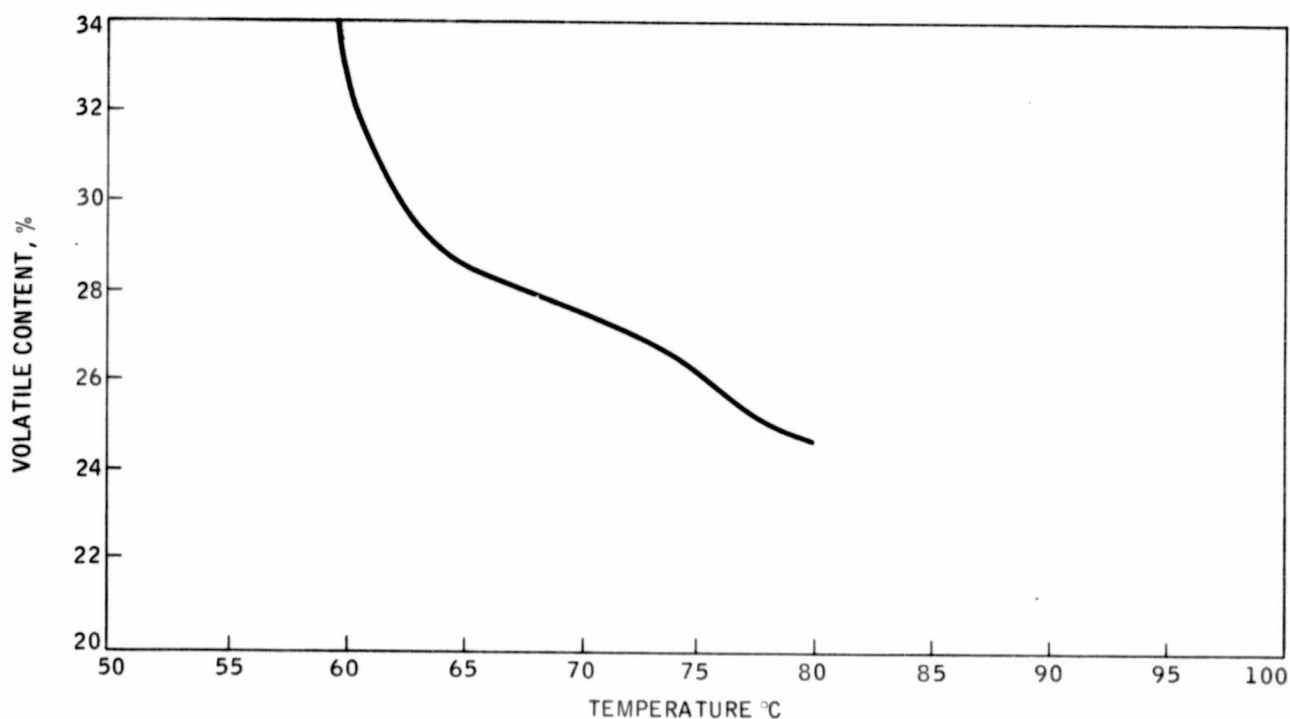


Figure 28. B-Staging Temperature; Effect on Residual Volatiles of 170-1 Polyimide Precursor

the volatile content of the 170-1 precursors. The data indicates that at temperatures below 65°C (150°F) B-staging becomes ineffective and results in resins with a high residual solvents; this type of precursors can produce very irregular foam structures. The volatile content decreases as the temperature increases to 76°C (170°F) and remains practically constant thereafter. Prepolymerization of this type of resin starts to occur at a temperature higher than 80°C (176°F). Therefore, the B-staging temperature was limited to a very narrow range. The safe range for the resin of the 170 series has been found to be between 65.5 and 76.7°C (150-170°F). It is at

this temperature that the most flexible and resilient foams have been produced from this resin system.

iii. Vacuum Heating

The 170-1 precursors prepared at a reaction temperature of 60-70°C (140-158°F) and B-staged at 65.5°C (150°F) were further processed under an absolute pressure of 33.4-3.3 kPa (1-10 in. Hg) at four different temperature conditions. These were:

60°C	(140°F)
65.5°C	(150°F)
71.1°C	(160°F)
76.7°C	(170°F)

Vacuum heating is the last, but very critical step in the preparation of the final polyimide precursors. In this step the volatile content of the precursors are adjusted to a level of 16-20 percent using process conditions which prevent excessive pre-polymerization of the precursors. Although the data we have collected by determination of the melting point and volatile content of the precursors has been of value in defining the foaming behavior of the precursors for screening of candidates, no determination of the molecular weight of these resins has been done. Solubility tests have indicated that incipient polymerization is occurring with all these resins, but the degree of polymerization is not known. This is a subject that will require investigations in future programs.

Figure 29 shows the evolution of volatiles for each of the temperature conditions under study. Polyimide precursors vacuum processed at a temperature of 60, 65.5 and 71.1°C yield resilient, flexible foams which possess homogeneous cellular structure, however, at 76.7°C the foams start to exhibit lower rise and possess more brittle cellular structures due to excessive pre-polymerization. On the basis of this study, the optimum temperature conditions for vacuum processing the 170-1 resin system were established. These conditions were a temperature of 65.6°C (150°F) at an absolute pressure of 23.3 kPa (6.9 in. Hg) for 30 minutes, followed by an additional 30 minutes at 16.5 kPa (4.9 in. Hg).

The B-staging and vacuum heating processes were also studied for the resin belonging to the 160 system, although only on a limited effort, since these foams have been found to be deficient in hydrolytic stability. For these resins the range of B-staging temperature was found to be 82.2-87.8°C (180-190°F) and that of the vacuum process was selected to be 76.7°C (170°F). The resins belonging to the 190 system have been excluded from this study.

The synergistic effect of all parameters evaluated in this and in previous sections has resulted in polyimide precursors of the 170 series with significantly improved properties. Using the optimized process conditions reported here, polyimide precursors have been prepared by modification with

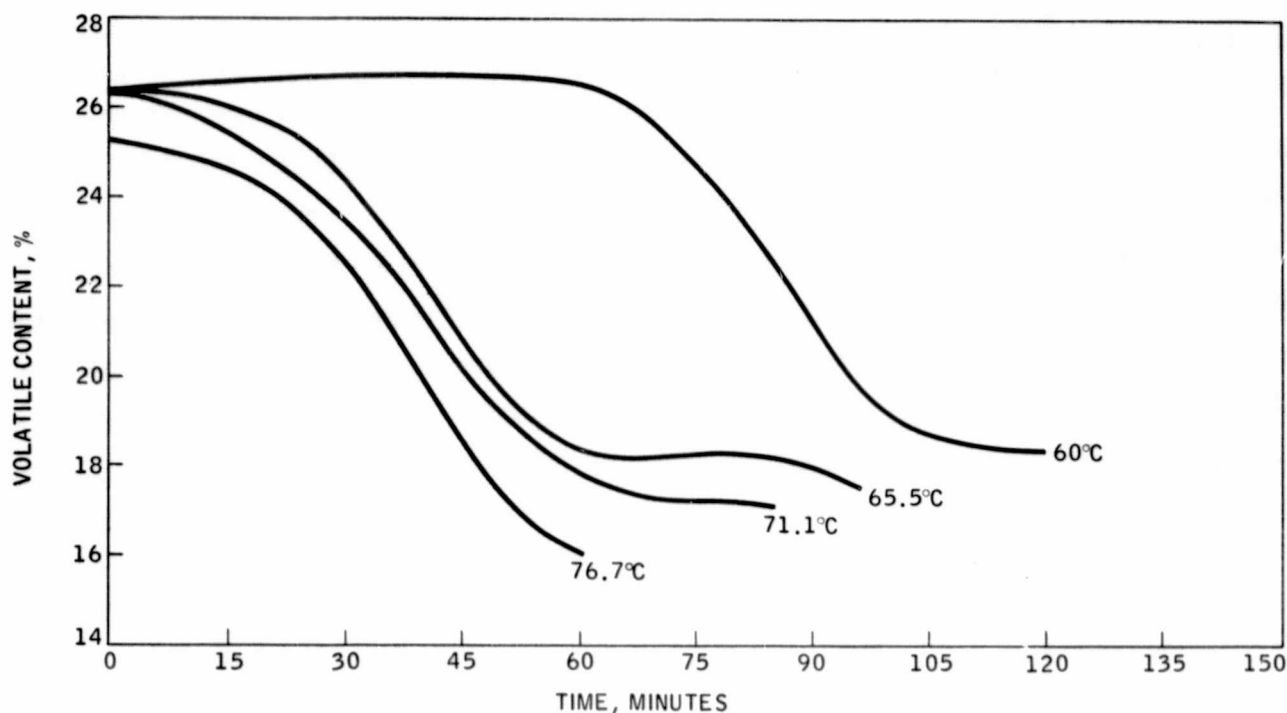


Figure 29. Time-Temperature; Effect on Volatile Content of 170-1 Foaming Resin Processed at Reduced Pressure

0.2% FSB, which have produced flexible resilient foams at a molar ratio of 2,6DAP as low as 0.1 as shown in Table XIII. The table presents a summary of the resin compositions, physical properties of the polyimide precursors and of the respective foams belonging to the 170 series. These precursors were prepared at a condensation reaction temperature of 60-65°C (140-149°F) for a period of five minutes followed by B-staging at a temperature of 65.5°C (150°F) for 16 hours. The final step was carried out by vacuum heating the precursors at 65.5°C (150°F) at an absolute pressure of 23.3 kPa (6.9 in. Hg) for 30 minutes followed by an additional 30 minutes at 16.5 kPa (4.9 in. Hg). These optimized conditions have been used for preparation of the modified or unmodified polyimide precursors evaluated in this task and in the tasks dealing with scale-up studies, characterization and selection of the candidate materials and fabrication of final samples for shipment to NASA-LBJ Space Center.

(2) New Foaming Methods

After the evaluation and selection of the optimum process parameters, part two was initiated to investigate new heating and foaming methods. The principal objective of this study was to overcome the deficiencies of convective heating which, due to the poor thermal conductivity of the foaming mass, produced non-homogeneous heat-transfer and consequently irregular cellular structure.

Table XIII
Polyimide Foam Precursors With Improved Reaction Conditions

Foam Resin Number	Composition	Molecular Ratio	M.P. °C	Volatile %	FSB Conc. %	Foam Characteristics
170-1-59	BTDA:2,6DAP:MDA	1:0.4:0.6	101-110	20.6	0.2	Flexible, resilient, good cellular structure
170-2-19	BTDA:2,6DAP:MDA	1:0.3:0.7	103-108	21.1	0.2	Flexible, resilient, very good cellular structure
170-7-1	BTDA:2,6DAP:MDA	1:0.25:0.75	98-105	20.7	0.2	Flexible, resilient, very good cellular structure
170-5-2	BTDA:2,6DAP:MDA	1:0.2:0.8	94-100	20.6	0.2	Flexible, resilient good cellular structure
170-6-2	BTDA:2,6DAP:MDA	1:0.1:0.9	94-102	20.6	0.2	Flexible, resilient, marginal cellular structure

The new foaming methods investigated were:

- i. Multi-Stage Techniques
- ii. Dielectric Heating
- iii. Microwave Heating

The initial phase of this study was conducted to prove the feasibility of each technique and to select candidate processes by comparing the foaming behavior of selected polyimide precursors. The selection of the candidate processes was done on the basis of data derived from the evaluation of small size foamed samples for cellular structure, flexibility, resiliency, and density. These properties have shown to influence the mechanical and dynamic characteristics of the foams (Ref. 1). In a second phase more advanced studies were carried out by scaling-up the selected processes in accordance with the plan. The three methods under study and the experimental results leading to the selection of candidate processes are described next.

i. Multi-Stage Techniques

The use of multi-stage foaming techniques to improve homogeneity of cellular structure was initiated utilizing the concept of vacuum influenced foaming. This process was carried out as described in Section 3.4. The apparatus consisted of a vessel contained within an oven and connected to a vacuum pump via a line and regulating valve. This system permitted foaming polyimide resins over a wide range of temperature and pressure. The procedure consisted of preheating the apparatus to the desired temperature followed by inserting the powder polyimide precursor. The vessel was closed and the pressure was reduced to the desired level by means of the vacuum pump. After a predetermined period of time, the pressure was normalized and the heating continued to cure the foam at atmospheric pressure.

The initial study involved little more than iterative experiments designed to approximate the conditions of temperature and pressure which produced the most desirable product. Figure 30 shows the effect of pressure on the density of the foams produced from FR 170-1 precursor at 287°C (550°F). Below an absolute pressure of 33.4 kPa (9.9 in. Hg) the evolution of volatiles occurred before the initiation of the foaming mechanisms, hence foam density increased. Above this pressure the foam density remained practically constant, but, as the pressure of the system approached atmospheric conditions, striations and non-homogeneous foam structure started to appear. This method offered a method to alleviate the problem of striations. In a continuation of the effort to improve cellular structure, a study was undertaken to evaluate the effect of surface active agents. The 170-1 polyimide precursors were prepared at a FSB surfactant concentration of from 0 to 0.8 percent based on polyimide solids and foamed at 287.7°C (550°F) and an absolute pressure of 67.1 kPa (19.9 in. Hg) for 15 minutes, followed by a final cure at 315°C (600°F) for an additional 15 minutes. Table XIV presents the data obtained from this study. As the concentration of the surfactant increased, the density of the foams decreased and the foam structure became significantly more homogeneous. At very high concentration of surfactant, however, more brittle foam structure was obtained which often collapsed into a higher density more rigid foam. The optimum FSB surfactant concentration for the conditions reported above was found to be between 0.2 and 0.4 percent.

This process produced polyimide foams with a more homogeneous cellular structure than those obtained by the conventional thermal processes, but more important, it avoided the formation of striations which was consistently observed in thermal processes. Figure 31 shows the improved cellular structure of a foam (FR-170-1) produced by vacuum techniques compared with that produced from the same resin by conventional thermal processes which is shown in Figure 32.

ii. Dielectric Heating

Dielectric processes provide one of the most reliable method of creating uniform heat through a plastic material which possesses sufficiently high loss factor. The heating process is achieved by converting electrical energy into heat energy by molecular friction of the material subjected to the high-frequency electrical field. This energy conversion takes place almost instantly throughout the mass of the material and therefore the heating effect is very uniform.

Preliminary foaming experiments utilizing dielectric heating were carried out by the Votator Division of Chemetron Corporation, Louisville, Kentucky, utilizing a Thermex Model TBGA High Frequency Generator operating at a nominal frequency of 27 MHz. This unit was shown in Figure 5, Section 3.4. The procedure used consisted of spreading the powder polyimide precursor to form a thin disk on a sheet of G-7 glass-silicone electrical insulating material and by heating it in the high frequency field established between two parallel plates in the Thermex High Frequency Generator.

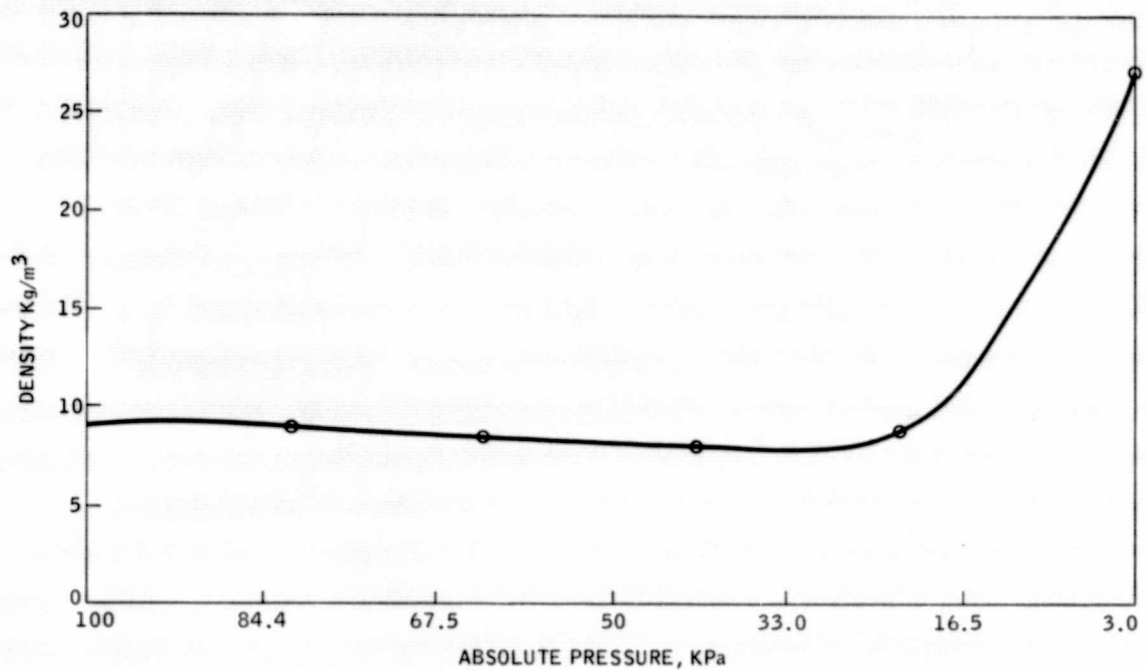


Figure 30. Multi-Stage Foaming; Effect of Pressure on Density (FR 170-1)

Table XIV

Multi-Stage Foaming; Effect of Surfactant Concentration on Polyimide Foams Derived From FR 170-1

FSB Concentration (%)	Absolute Pressure kPa	Foam Density		Resilient Ball Rebound	Cellular Structure Striations
		lbs/ft ³	kg/m ³		
0	67.1	1.20	19.22	50	Present
0.2	67.1	0.53	8.49	60	Minimal
0.4	67.1	0.73	11.69	65	None
0.6	67.1	0.76	12.17	60	None
0.8	67.1	0.98	15.69	40	None

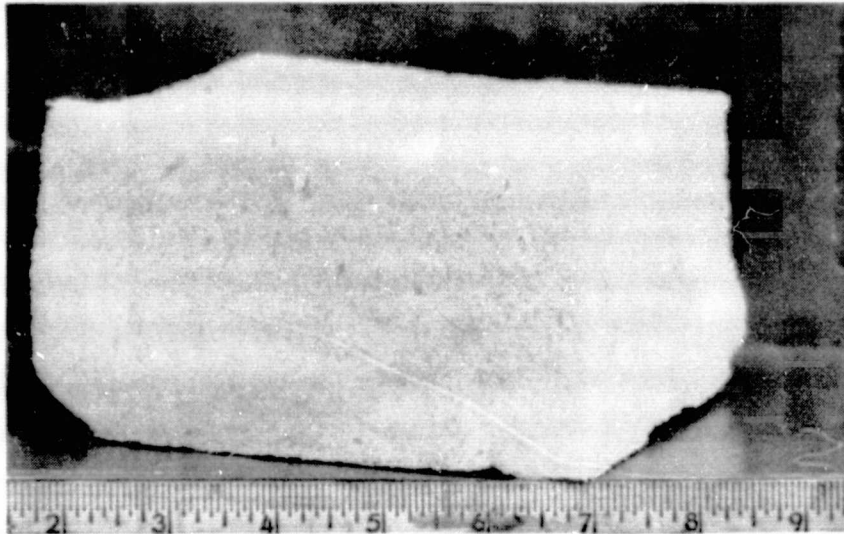


Figure 31. Foaming by Vacuum Processes (FR 170-1)

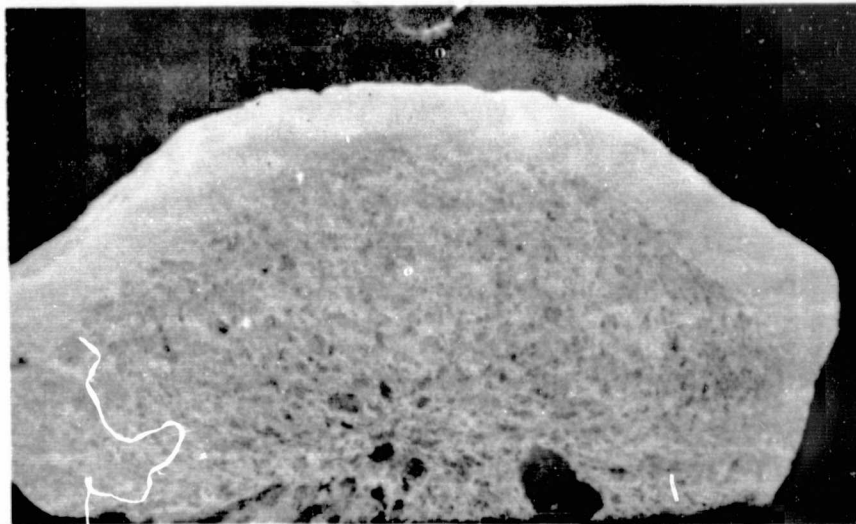


Figure 32. Foaming by Thermal Processes, FR 170-1

At the conclusion of these exploratory tests, data was derived which proved the feasibility of the concept. It was found that the polyimide powder precursors did not heat readily in a high frequency field when the material enters the field at room temperature, however, the same precursor in contact with a surface with a temperature as low as 250°F started to expand and absorb energy very readily. The cell structure developed by the rapid expansion was not uniform. Additionally the high frequency heating alone, did not heat the expanded foam to the temperature required for curing so that an additional post-heating cycle in a circulating air oven at 287.7-315°C (550-600°F) was necessary to complete the curing process. This produced two stages of expansion; one during the high frequency heating and an additional, but much lower expansion, during the post-heating cycle.

Although this additional heating cycle was not objectionable, the cell structure developed during the two stages of expansion was separated by a densified area or striation similar, but not as pronounced, as that obtained using thermal processes. A programmed application of the high frequency energy may have produced a less rapid foam rise and minimized the striations occurring during the post-heating cycle, however, no facilities were available for this type of test. This is still a viable process for foaming polyimide resins, but it will require more effort than it would be possible within the scope of this program to optimize the technique.

iii. Microwave Heating

Microwave heating processes offer the most advanced method of heating a material which is reactive to electromagnetic radiation. Heating is achieved by means of the energy generated when the molecular content and arrangement of materials couple with the microwave field producing vibration of reactive groups. This effect causes an increase of the temperature of the mass due to molecular friction, the higher the temperature rise the more effective the microwave interaction. This heating effect is the most uniform and homogeneous and directed away from the center of the mass, therefore, temperature gradients or transfer losses are reduced to an absolute minimum.

Since speed, efficiency and uniformity of heating are considered to be the most important factors in achieving uniform cell structure, this process was expected to significantly improve the foaming mechanism of the polyimide foam precursors.

Preliminary foaming studies were carried out by Gerling Moore Inc., Palo Alto, California, using a Model 4115 Precision Microwave Cavity operating at a nominal frequency of 2450 MHz and a power of 2.5 and 5 kW and shown in Figure 4.

The process used consisted of spreading about 10 g of the polyimide precursor to form a thin disc about 0.6 cm (0.25 in.) thick on a sheet of Teflon. The powder was preheated by conduction to approximately 150°C (302°F) and placed in the microwave cavity for foaming. The expansion in the microwave field was very rapid, the cellular structure developed very uniform, the cell size very small throughout the foaming mass.

In this study it was found that the applied microwaves readily heat and foam small samples of polyimide precursors only if the powder was preheated, but larger samples reacted to microwaves and expanded even at room temperature. The expansion appeared to be more rapid with the 5 kW microwave power, but in all cases the applied microwaves alone did not heat the expanded mass to the temperature required for curing. Consequently, an additional post-heating cycle was required. This was accomplished by heating the foams in a circulating air oven at 287.7-315°C (550-600°F). This additional heating period did not produce a second expansion and did not alter the original cellular structure.

At the conclusion of this preliminary study microwave heating proved the most suitable method for foaming polyimide resins. A preliminary process was developed which permitted producing larger foam sheets. The process consisted in spreading 0.5-1.0 cm (0.2-0.4 in.) thick polyimide powder precursor over an area of approximately 400 cm² (64 in.²) on a Teflon sheet. The powder was preheated in a circulating air oven at 204.4-260°C (400-500°F) for 1-3 minutes and then placed in the microwave cavity for 2 to 5 minutes. The expanded mass was postcured in a circulating air oven for 10-30 minutes at 204.4°C (400°F) followed by 10-30 minutes at 260°C (500°F) and 30 minutes at 287.7°C (550°F). Samples of foams produced by this process are shown in Figure 33(a) and 33(b). Figure 33(a) is a resilient foam produced from 170-2 resin and Figure 33(b) shows a thermal acoustical insulation foam at a density of 4.8 Kg/m³ (0.3 lbs/ft³) produced from 0.2% FSB modified 170-2 resin. This procedure served as the basis for the study of process parameters and scale-up processes as it will be discussed next.

4.1.3 Scale-up Processes

This paragraph is divided into three parts to improve clarity. The first part (1) covers the study of scale-up by thermal processes followed in order by multi-stage techniques (2) and microwave heating (3). The major emphasis of this task is to develop processes for fabrication of large specimens to overcome foam deficiencies in at least three areas: fatigue strength, resistance to high humidity and production cost. Emphasis was placed upon three major parameters for each of the processes. These were: mass and thickness effect, heating cycles, and effect of additives on foam properties. Resins belonging to the 170 systems were used for these studies.

(1) Scale-Up Processes by Thermal Methods

Foaming by thermal processes, also called free rise techniques, has been used at Solar from the start of the development of polyimide foams and has been covered in a previous report (Ref. 1). The study has been continued in the present program in accordance with the plan. Table XV presents a summary of the study of mass and thickness effect carried out with FR 170-1 polyimide precursors modified with 0.2% FSB. The precursors were foamed for 15 minutes at 260°C (500°F) and 15 minutes at 287.7°C (550°F). Table XVI presents the summary of results obtained from the study of evaluation of curing cycles using the same resin composition. In these experiments the powder precursor was spread over an area of 25.0 x 25.0 cm (10 x 10 in.) at 0.23 mm thickness. The effect of additives on the foaming behavior of the 170 series was reported in Section 4.1.1 and FSB was selected as the optimum candidate for foaming. During the present study of thermal foaming no attempts were made to re-evaluate these additives, suffice to say that 170-1 polyimide precursors, made without FSB surface active agent, gave very poor cellular structure, large voids and in many instances very irregular rise when foamed in large sizes.

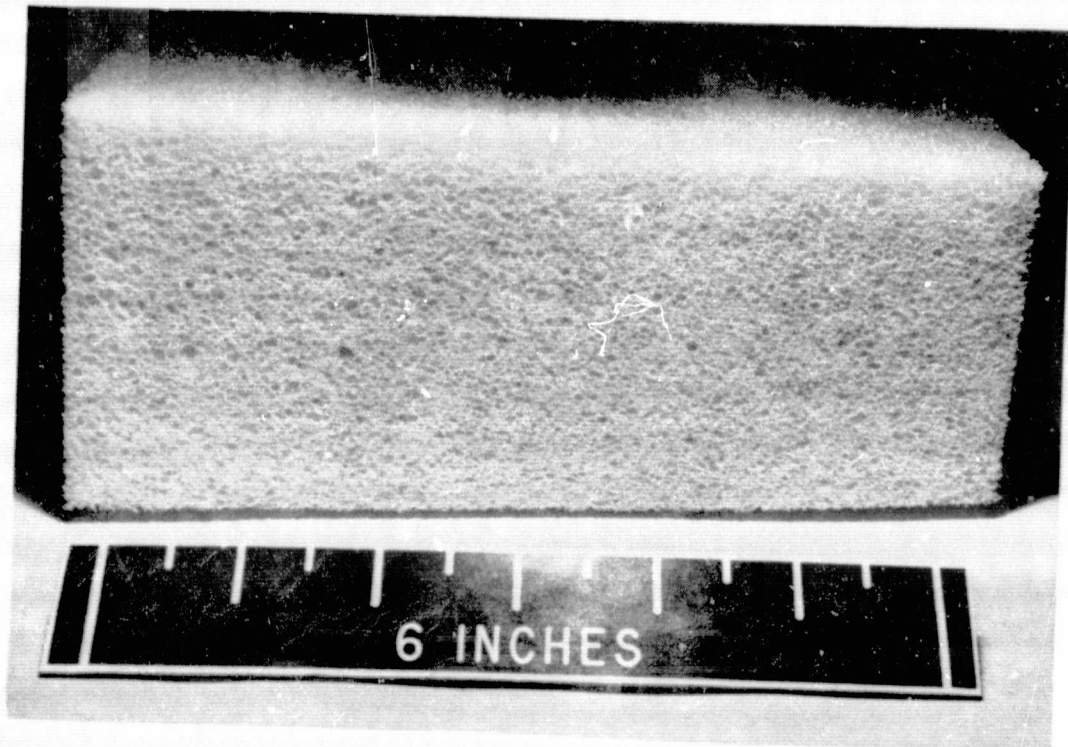


Figure 33a. Resilient Polyimide Foam by Microwave Foaming (170-2)

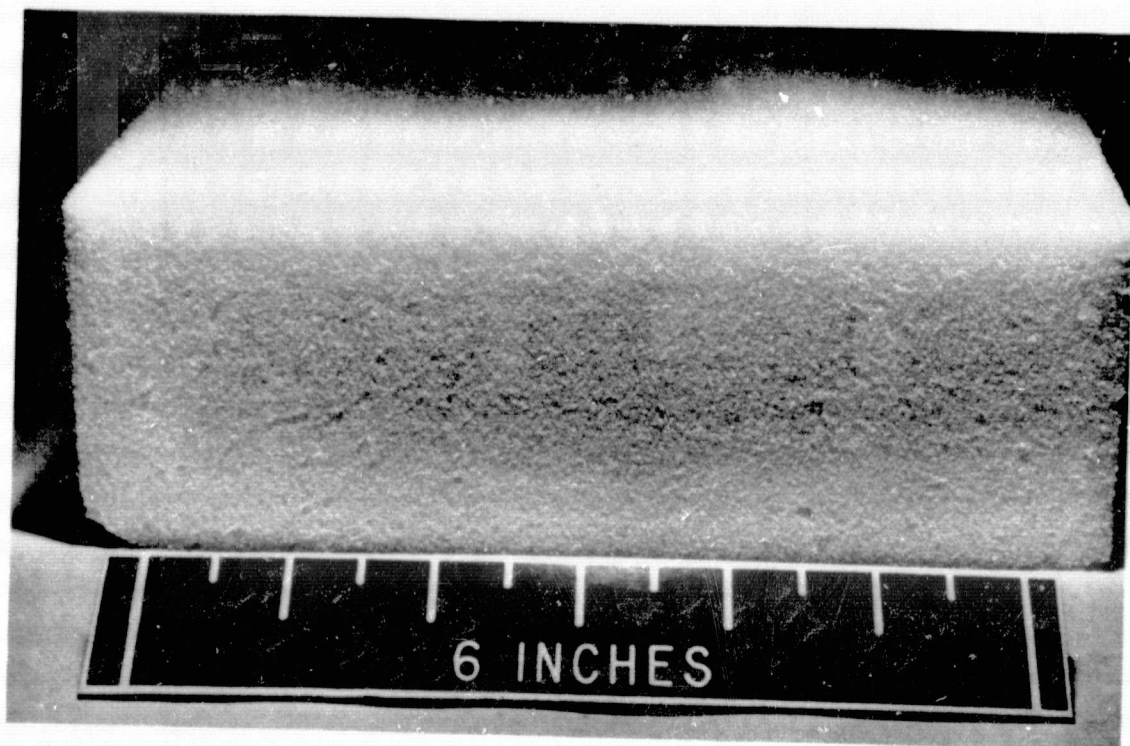


Figure 33b. Thermal Acoustical Polyimide Foam by Microwave Foaming (170-2, 0.2% FSB)

Table XV
Thermal Foaming of 170-1 Resin
Mass and Thickness Effect

Powder Precursor Coating Size		Foam Properties		
Area mm	Thickness mm	Resiliency	Density kg/m ³	Cellular Structure
250 x 250	1.57	40	19.5	Slightly brittle, no striations
250 x 250	2.3	75	18.5	Homogeneous, striations
250 x 250	3.1	60	17.2	Irregular, striations
250 x 250	3.7	55	16.4	Very irregular, striations

Table XVI
Thermal Foaming of 170-1 Resin; Temperature Effect

Temperature		Curing Cycle Time, Minutes	Foam Properties		
°C	°F		Resiliency	Density kg/m ³	Cellular Structure
315	600	30	45	24	Foam collapse
287.7	550	45	65	16.0	Homogeneous, striations
260/287.7	500/350	15/30	60	17.6	Marginally homogeneous, striations
232.2/287.7	450/550	15/30	50	19.8	Irregular - striations

This study revealed significant developments regarding the foaming behavior of the 170 system. First of all, there was not evidence of chain terminating reactions occurring during foaming as it was experienced with other systems (Ref. 1); secondly, precursors of the 170 system can be foamed and cured at a temperature as low as 260-287.7°C (500-550°F). Results have shown that the optimum powder thickness for fabrication of large specimens by thermal processes is between 2.3 and 3.1 mm (0.092-0.125 in.) and that the curing cycle as well as the powder thickness affected not only the cellular structure, but also the mechanical properties of the foams.

This phase of the program included studies of alternative methods of foaming by using restricted molds to produce foams having defined shapes or by cutting these shapes from blocks of foams. Studies of foaming in restricted molds were performed in a mold design which consisted of a perforated steel

plate covered with 181 style glass cloth on top of which was placed a 25.0 x 25.0 x 0.75 cm (10 x 10 x 3 in.) aluminum frame. The top of the frame was closed with a perforated plate covered with 181 style glass cloth. This configuration permitted fabrication of foams of predetermined shape and density. Foaming was accomplished by laying the powder in the mold and allowing it to expand at 287.7°C (550°F) in a circulating air oven. The foams expanded to the exact shape of the mold. This compression technique produced foams with poor flexibility and resiliency, probably caused by poor heat transfer of the mold. Better heating techniques could overcome this deficiency.

An alternative method for fabrication of shaped foam samples consisted in cutting slabs of foams to exact dimensions. This was done with bandsaw, friction and hot-wire techniques. All methods worked to satisfaction. Hot-wire techniques are presently used to cut polyurethane foams for production of seat cushions for use in aircraft applications.

(2) Scale-Up Processes by Multi-Stage Techniques

The fabrication of large specimens by vacuum influenced methods was hampered by the small size of the pressure vessel used in the study.

The most important parameter studied in this phase was the effect of pressure on the cellular structure of the foams. All tests were conducted with FR 170-1 modified with 0.2% FSB. Table XVII presents a summary of the results obtained from this study. The data show that the cellular structure and formation of densified areas in the foaming mass are dependent upon the pressure used during foaming. As the pressure is reduced from atmospheric, the formation of densified areas is less pronounced, the cellular structure more uniform and the density decreases. As the pressure is further reduced the foaming behavior is altered again with formation of less resilient foam and finally foam collapse. Large samples 20 x 20 cm (8 x 8 in.) were produced by foaming FR 170-1 modified with 0.2% FSB at a temperature of 287.7°C (550°F) and an absolute pressure of 67.1 kPa (19.9 in. Hg) followed by postcuring at 287.7°C (550°F). In general, the flexibility, resiliency and cellular structure of foams produced by multi-stage techniques were superior to those produced by thermal processes. This comparative study was made with the resin precursors shown in Table XIII. Figure 34 shows foaming behavior of the precursors reported in Table XIII processed by vacuum influenced techniques. From right to left are foams made with FR 170-1 through FR 170-6 showing the lower foam rise as the ratio of the heterocyclic diamine decreases. Foaming by multi-stage techniques has been considered a candidate process for preparation of large specimens.

Table XVII
Multi-Stage Foaming
Effect of Pressure on the Foaming Behavior of FR 170-1

Absolute Pressure		Foam Properties		
kPa	in. Hg	Resiliency	Density kg/m ³	Cellular Structure
100.9	29.9	50	9.28	Marginally homogeneous, striations
84.0	24.9	45	9.12	Homogeneous, no striations
67.1	19.9	55	8.8	Homogeneous, no striations
50.3	14.9	50	8.32	Marginally homogeneous
33.4	9.9	40	8.96	Very irregular
16.5	4.9	30	27.2	Collapsed structure

Table XVIII
Surfactants; Effect on Density and Resiliency of Foams Derived
From 170-1 Precursors by Microwave Heating

Surfactant Concentration (%)	Coating Thickness (mm)	Preheat Temperature (°C)	Time Seconds	Density		Resiliency
				kg/m ³	lb/ft ³	
0	0.95	204	180	7.4	0.46	90
0	0.76	204	165	7.0	0.44	90
0	0.64	204	150	6.7	0.42	90
0.2	0.95	204	180	4.8	0.3	40
0.2	0.76	204	180	4.9	0.31	40
0.2	0.64	204	120	7.2	0.45	40



Figure 34. Multi-Stage Technique; Foam Rise of Precursors With Decreasing 2,6DAP Molar Ratio. From right to left; 170-1 (0.4:0.6), 170-2 (0.3:0.7), 170-7 (0.25:0.75), 170-5 (0.2:0.8), 170-6 (0.1:0.9)

(3) Scale-Up Process by Microwave Heating

The investigations dealing with processes to fabricate large specimens by microwave heating were carried out using a Model 4110 Batch Microwave Cavity leased from the Gerling Moore Corporation. This unit is similar in size to the Model 4115 except that it operates at a power of 2.5 kW. The unit with a foamed sample is shown in Figure 4. The most critical parameters selected for this study were:

- i. Pre-heat Temperature
- ii. Coating Thickness
- iii. Effect of surface active agents

The technique consisted of preheating the powder prepolymer coated on a Teflon sheet to the desired temperature for predetermined period of time followed by foaming in microwave oven. Samples were subsequently post-heated and cured. The foams were then cut and inspected for cellular structure and mechanical properties. A discussion of the effects of the critical process parameters is presented below.

i. Effect of Pre-Heat Temperature

Pre-heating makes the polyimide powder more reactive to the microwave field causing a higher temperature rise of the mass and higher foam rise. This study was carried out by preheating the powder at 93.3°C (200°F), 148.8°C (300°F), 204.4°C (400°F), and 287.7°C (550°F) and room temperature. Figure 35 shows the effect of preheat temperature on the density of foams produced from FR 170-1 resin using a powder thickness of 0.5 cm (0.2 in.). At room temperature no foaming occurred, foam rise started thereafter and the density decreased with increasing pre-heat treatment. A temperature higher

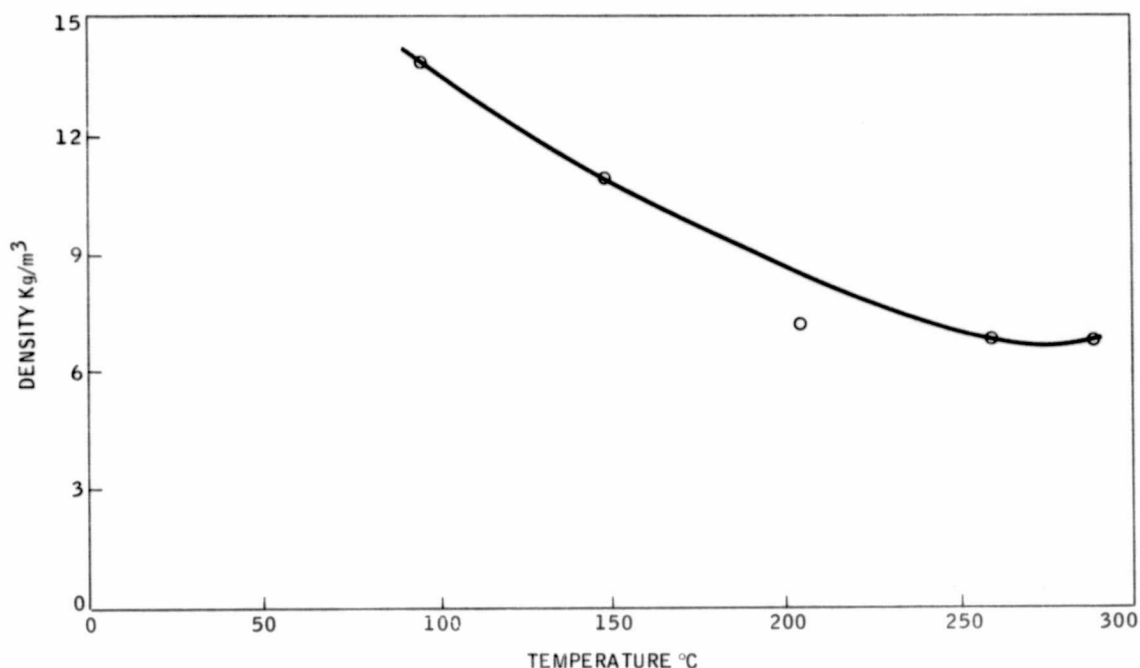


Figure 35. Microwave Foaming; Effect of Preheat Temperature on Density (FR 170-1)

than 260°C (500°F) produced pre-foaming and prepolymerization of the precursors and non-homogeneous cellular structure. From this study a temperature of 204.4°C (400°F) for a period of time of 150-200 seconds was selected for the subsequent study.

ii. Effect of Coating Thickness

This study was carried out by coating the FR 170-1 resin on a Teflon sheet over an area of 25 x 25 cm (10 x 10 in.) followed by preheating the powder at 204.4°C (400°F) and foaming in the microwave oven. Figure 36 shows the vertical rise of foams derived from FR 170-1 precursors at increasing powder thickness of 0.25, 0.5, 0.75 and 1.0 cm (0.1, 0.2, 0.3, 0.4 in.) (left to right) when the precursors were preheated at 204.4°C (400°F). Figure 37 shows the same resin at the same coating thickness foamed in the microwave cavity without the preheat cycle; in this case the resins are less reactive and completely unreactive when a powder thickness of 0.25 cm (0.1 in.) was used. These figures show that two factors influence the rise of resins foamed in a microwave field. These are, coating thickness and preheat temperature. These two parameters have shown to have a synergistic effect on the foam rise and cellular structure. From this study a coating thickness of approximately 1.0 cm (0.4 in.) was selected for preparation of large specimens.

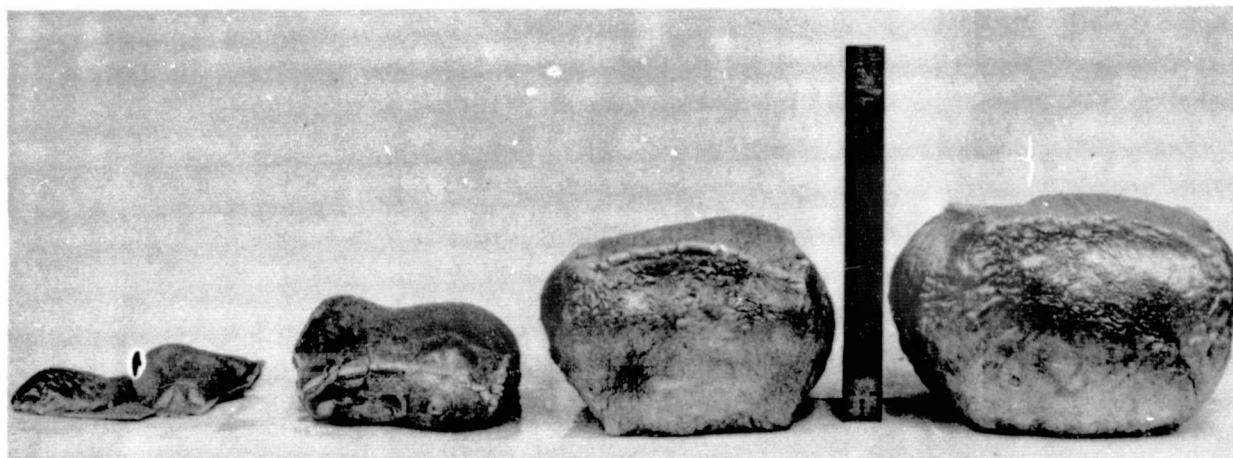


Figure 36. Microwave Foaming; Effect of FR 170-1 Precursor Thickness on Foam Rise With Pre-Heat Cycle. Powder Thickness; 0.25 cm, 0.5 cm, 0.7 cm, 1.0 cm (left to right)

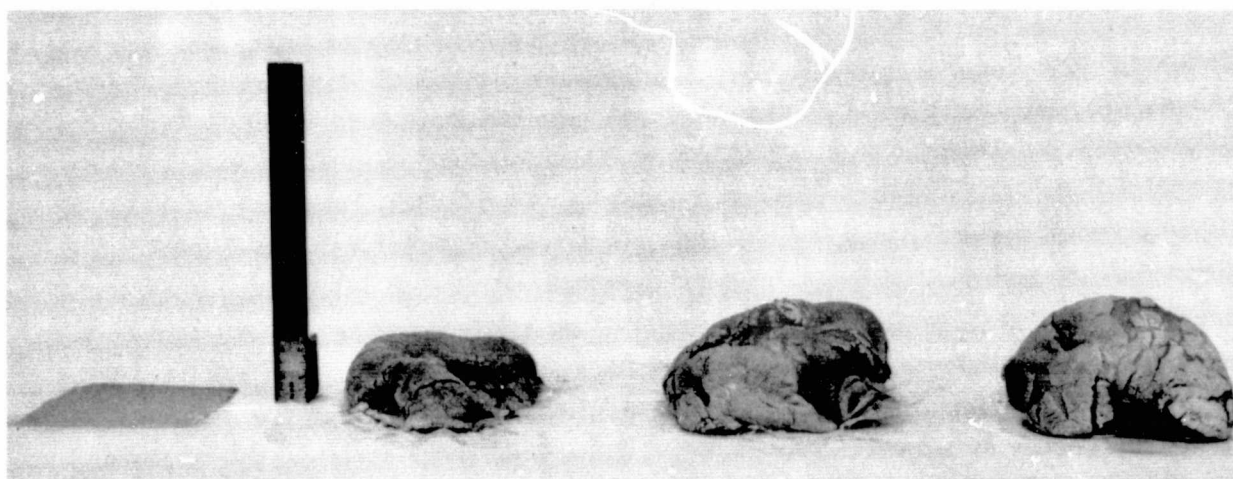


Figure 37. Microwave Foaming; Effect of FR 170-1 Precursor Thickness on Foam Rise Without Pre-Heat Cycle. Powder Thickness; 0.25 cm, 0.5 cm, 0.75 cm, 1.0 cm (left to right)

iii. Effect of Surface Active Agents

In this study the surface active agent evaluated was FSB at a concentration of 0.2 percent based on polyimide solids. This concentration was selected previously in the study of the effect of surface active agents on foams produced by thermal processes. Table XVIII and Table XIX show the effect of FSB on foams derived from 170-1 and 170-2 resins at various precursor thicknesses and a preheat temperature of 204°C (400°F). The most significant finding derived from this study relates to the improved

Table XIX
Surfactants; Effect on Density and Resiliency of Foams Derived
From 170-2 Precursors by Microwave Heating

Surfactant Concentration (%)	Coating Thickness (mm)	Preheat Temperature (°C)	Time Seconds	Density		Resiliency
				kg/m ³	lbs/ft ³	
0	0.95	204	180	7.8	0.49	80
0	0.64	204	150	7.2	0.45	80
0.2	0.95	204	190	8.5	0.53	30
0.2	0.64	204	160	8.6	0.54	30

resiliency and flexibility of foams produced by microwave foaming polyimide precursors containing no surfactants. This contrasts with the data found thus far from the study of the other foaming methods where a surface active agent was found to be necessary to achieve flexibility and resiliency. Foams produced by microwave heating 170-1 and 170-2 precursors containing 0.2 percent FSB possessed lower density and a very fine and very homogeneous cellular structure. These characteristics are important in the selection of candidates for use in thermal acoustical insulation foams as it will be discussed later.

At the conclusion of this study two candidates were selected. These were FR 170-1 and FR 170-2 which contained no additives or surfactants. These two resins were subjected to final screening by determination of fatigue properties, hydrolytic stability and cost to select a final candidate. Fatigue tests were carried out in accordance with ASTM D-1564 Procedure B by flexing the test specimens for a total of 10,000 cycles (20,000 flexes) using the test apparatus shown in Figure 14. A total of 15 samples were tested to select foaming conditions which yielded optimum cellular structure. The hydrolytic stability of the material was tested by determination of loss of indentation load deflection after seven days at 73.9°C (165°F) in accordance with ASTM D-1564, Method A. The cost of each product was computed from the most recent prices of the raw materials purchased in development quantities for use in this program as shown in Table XX.

Table XXI shows a summary of this screening study. Resin 170-1 was selected as the final candidate for characterization and fabrication of samples for submittal to NASA-LBJ Space Center. This selection was made based on the comparative data obtained for the two resins and the final candidate selected on the basis of IDL loss upon exposure to high humidity, although fatigue characteristics appeared to be comparable and cost data more favorable for the 170-2 resins.

Table XX
Raw Material Cost of Final Candidates 170-1 and 170-2

Material Code	Cost/lb \$	170-1		170-2	
		Weight Charge lbs	Cost \$	Weight Charge lbs	Cost \$
BTDA	3.0	322.2	966.6	322.2	966.6
2,6DAP	12.0	43.5	522.0	32.6	391.2
MDA	1.45	119.5	173.7	139.2	201.8
Ethanol	0.25	190	47.5	190	47.5
Total Cost, \$			1709.8		1607.1
Foam Yield, lbs			449.2		494.0
Foam Cost, \$/lb			3.80		3.25

4.1.4 Characterization of the Candidate Polyimide Foam

The characterization of the final candidate was conducted using samples produced by foaming the 170-1 resin by microwave heating. Summary of the results is given in Table XXII.

Table XXI
Flexible, Resilient Foams: Final Screening of Candidates

Resin Number	Composition BTDA:2,6DAP:MDA	Density		Fatigue		Humidity Loss ILD %	Cost \$/lb
		lbs/ft ³	Kgm ³	Loss ILD %	Loss Thickness %		
170-2 (67 M)	1:0.3:0.7	0.71	11.4	4	22	20.1	3.25
170-2 (67 M)	1:0.3:0.7	1.0	16.0	67	24		3.25
170-1 (65 M)	1:0.4:0.6	0.74	11.8	28	39	7.5	3.80
170-1 (72 M)	1:0.4:0.6	1.1	17.6	3	24	-	3.80

Table XXII
Summary of Results. Flexible Resilient Foams
170-1 Resin

Property	ASTM Method	Units	Goal	Actual
Density	D-1564	Kg/m ³ lbs/ft ³	40.0 2.5	19.2 1.2
Tensile Strength	D-1564	N/m ² psi	82.7 x 10 ³ 12.0	92.4 x 10 ³ 13.4
Elongation	D-1564	%	30-50	39
Tear Resistance	D-1564	N/m lbs/inch	175.1 1.0	210.0 1.2
Indentation Load Deflection 25%	D-1564	N/3.2 dm ² lb-force/50 in ²	111.2-155.6 25-35	164.0 37.0
65%		N/3.2 dm ² lb-force/50 in ²	667-1112.0 150-250	1260.0 283.0
Compression Set 50%	D-1564	% Loss	7-10	6.2
Corrosion	PTMS No. 151		None	No Evidence
Resilience Rebound Value	D-1564	%	50 min.	75
Dry Heat	D-1564	% Loss Tensile Strength	20 max.	10.3 (increase)
Humidity 73.9°C (165°F) 100% R.H.	D-1565	% Loss IDL	20 max.	7.5
Fatigue 10,000 cycles 20,000 cycles	D-1564	% Loss IDL	20 max. 20 max.	14.0 24.0
Odor			None	Not detectable
Oxygen Index	D-2863	% Oxygen	40 min.	45
Smoke Density DS uncorrected	NBS	Optical density	30-50 max.	1.0
Thermostability	Thermogravimetric Analysis	Loss 204°C (400°F)	None	No loss
Toxic Product of Combustion HCl HF SO ₂ H ₂ S		10 ppm max. 10 ppm max. 10 ppm max. 10 ppm max.		None present None present None present None present

4.1.5 Fabrication of Samples for Submittal to NASA-LBJ Space Center

The foam specimens were prepared by spreading a 1.0 cm (0.4 in.) thick layer of the 170-1 polyimide precursor over an area 30.5 x 30.5 cm (12 x 12 in.) on a Teflon sheet (0.15 cm, 0.062 in. thick). Foaming was carried out in the microwave oven for 5 minutes followed by post curing at 260°C (500°F) and 287.7°C (550°F) for 30 minutes respectively. The outer skin was removed and the foam was cut to size. A total of 2.7 m² (3.2 sq yards) of the foam 7.6-12.7 cm thick (3-5 in.) will be delivered to NASA-LBJ Space Center in Houston, Texas.

Attempts were made to fabricate larger samples, but the foams obtained possessed poor cellular structure and non-homogeneous rise. These deficiencies are expected to be overcome with a more efficient microwave oven operating at a power output of 5 to 10 kW. This improved oven is recommended for future studies.

4.2 LAMINATE FLOOR AND WALL PANELING

This section covers the work dealing with optimization and characterization of low weight, rigid, polyimide foam structures for use in floor and wall paneling to protect habitable and cargo compartments of commercial aircraft from fuel fires. The studies undertaken in this task start with a very brief review of hardware requirements for fabrication of large panels (Section 4.2.1) followed by evaluation and screening of resins, fillers, and reinforcements (Section 4.2.2). The most promising resin/filler systems are then further optimized by investigation of improved process parameters, and new panel configurations (Section 4.2.3), followed by preparation and screening of candidate materials (Section 4.2.4), advanced testing (Section 4.2.5) and preparation of samples for NASA-LBJ Space Center (Section 4.2.6).

LAMINATE FLOOR PANELING

4.2.1 Tooling

This task involves the study pertinent to large panel construction. Initial lay-up of the resin-filler mixture was done on sheet of 0.158 cm (0.063 in.) aluminum covered with foil. These sheets were also used to support the panel during the foaming process. The foamed panels were compressed between two sheets of titanium alloy coated with MS-136 release agent in an electrically heated press with platen dimensions of 61 x 101 cm (24 x 40 in.). These facilities were used to fabricate large panels (55 x 85 cm, 22 x 34 in.) for testing and for submittal of final samples to NASA-LBJ Space Center.

4.2.2 Resin and Reinforcement Study

The purpose of this phase of the program was to screen and select the most promising resins and reinforcements for use in fabrication of floor and wall panels. The selected compositions were further studied by chemical alteration and by the use of new mechanical configurations to improve the properties most critical for the intended applications.

Studies have been previously undertaken at Solar Research Laboratories to improve the strength of polyimide rigid cellular materials. The most effective methods were found to be those employing the use of short fiber filled resins, which when foamed produced structures having improved mechanical properties at moderately low density. A second approach involved filling commercially available structures, such as honeycombs, with low density polyimide foams to produce materials meeting mechanical characteristics.

The studies dealing with selection of the resin systems is covered next in sub-section (1) followed by the selection of the reinforcements (2) and studies of new configurations (3).

(1) Evaluation of Polyimide Resins

The resins investigated under this phase of the program were prepared as reported in Section 3.3 and are reported below for each of the series under study.

Series E-160	160-0, 160-1, 160-2, 160-3, 160-4, 160-5
Series E-170	170-0, 170-1, 170-2, 170-3
Series E-190	190-0, 190-1, 190-2, 190-3

From this list, candidate resins which contributed to higher mechanical properties of a filled system were selected. The filler used in this screening study was 1.25 cm (0.5 in.) chopped carbon mat Grade VMC produced by Union Carbide. The most critical parameter selected to screen the candidate systems was compressive strength by means of compressive strength-density relationships. Although this was used as the primary test criteria, attention was also paid to bending strength, foam structure and fire hardening characteristics. The results of this study are discussed below for each resin systems in the sequence 160, 170, and 190. All curves shown were obtained by polynomial fitting of 4 to 6 data points using a computer aided program and no attempts were made to characterize this data by regression analysis.

160 Series

The strength-density relationship for the six resins of this series is shown by means of the curves of Figure 38. All the curves are very similar, indicating a close similarity in the properties of the resins. Resin 160-3 gave the highest tested strength and 160-5 showed what appears to be the best strength-density relationship. Therefore, these two resins were selected as candidates from the 160 series.

170 Series

The strength-density relationship for the E-170 resins is shown by means of the curves of Figure 39. At a density level of 250 kg/m^3 and below, two resins, 170-2 and 170-3, are clearly superior as shown by their higher strength to density ratio relative to the other two resins. Therefore 170-2 and 170-3 were selected from this series.

190 Series

Figure 40 shows the strength-density relationship for this series of resins. Two of the resin systems behaved rather erratically as shown by the

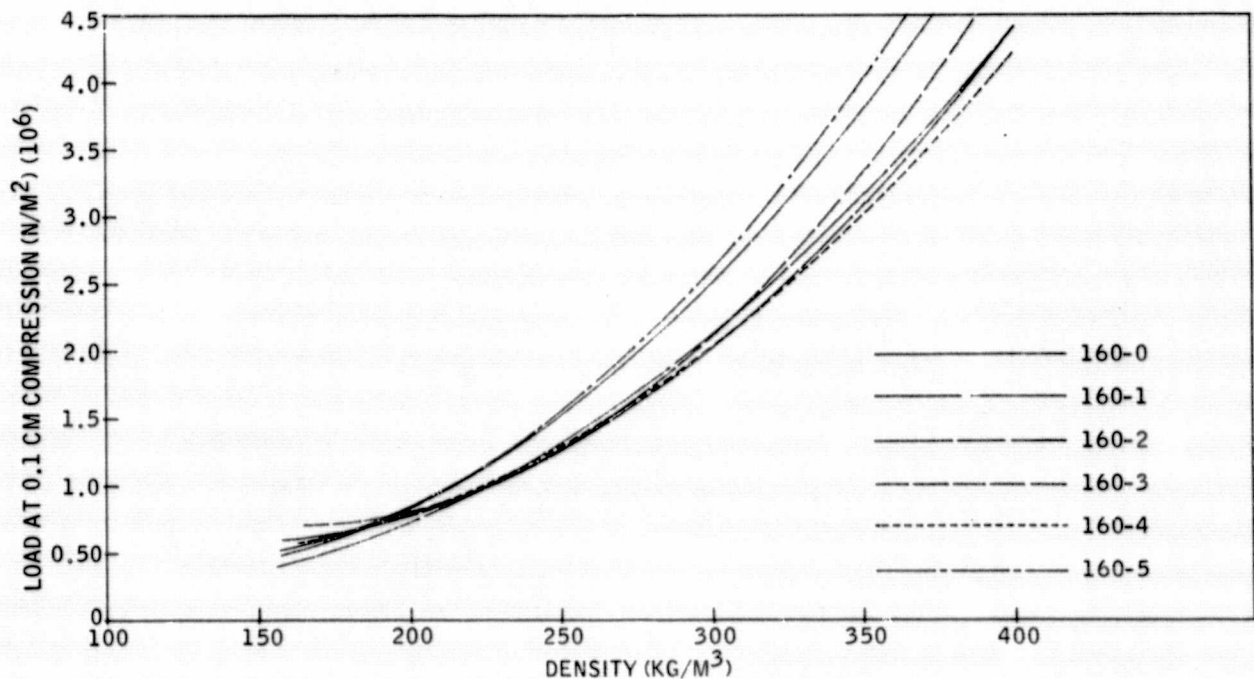


Figure 38. Compressive Strength of 160 Series Resins Filled With Chopped Carbon Mat

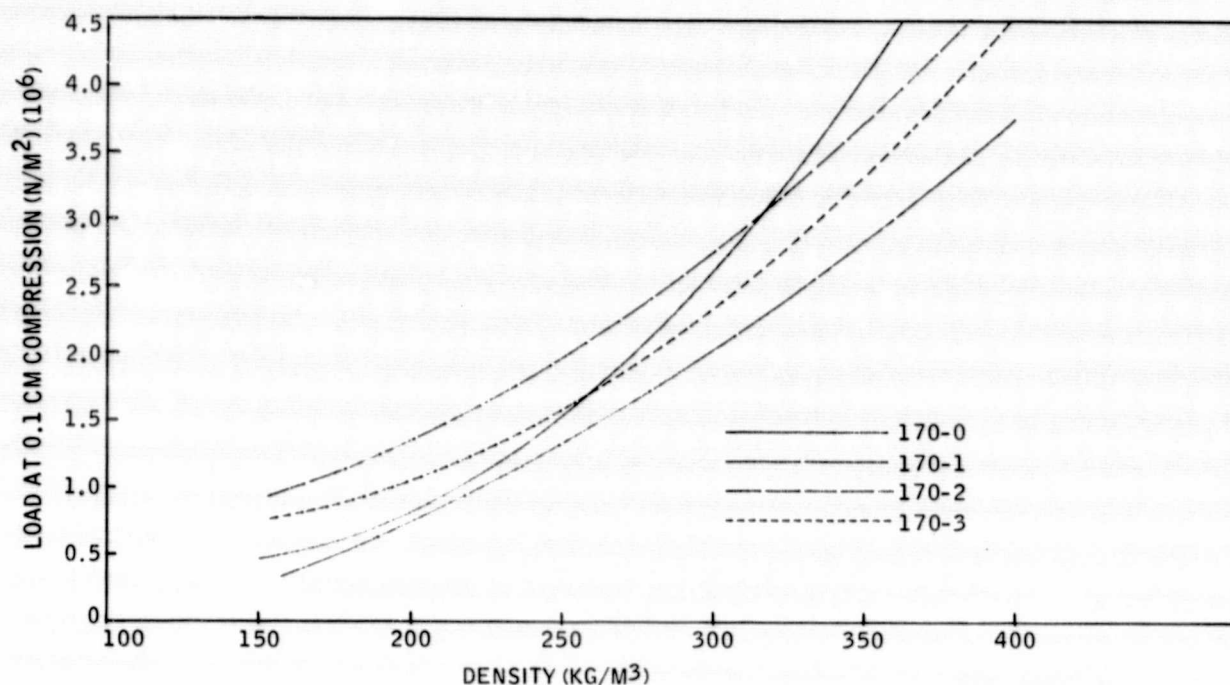


Figure 39. Compressive Strength of 170 Series Resins Filled With Chopped Carbon Mat

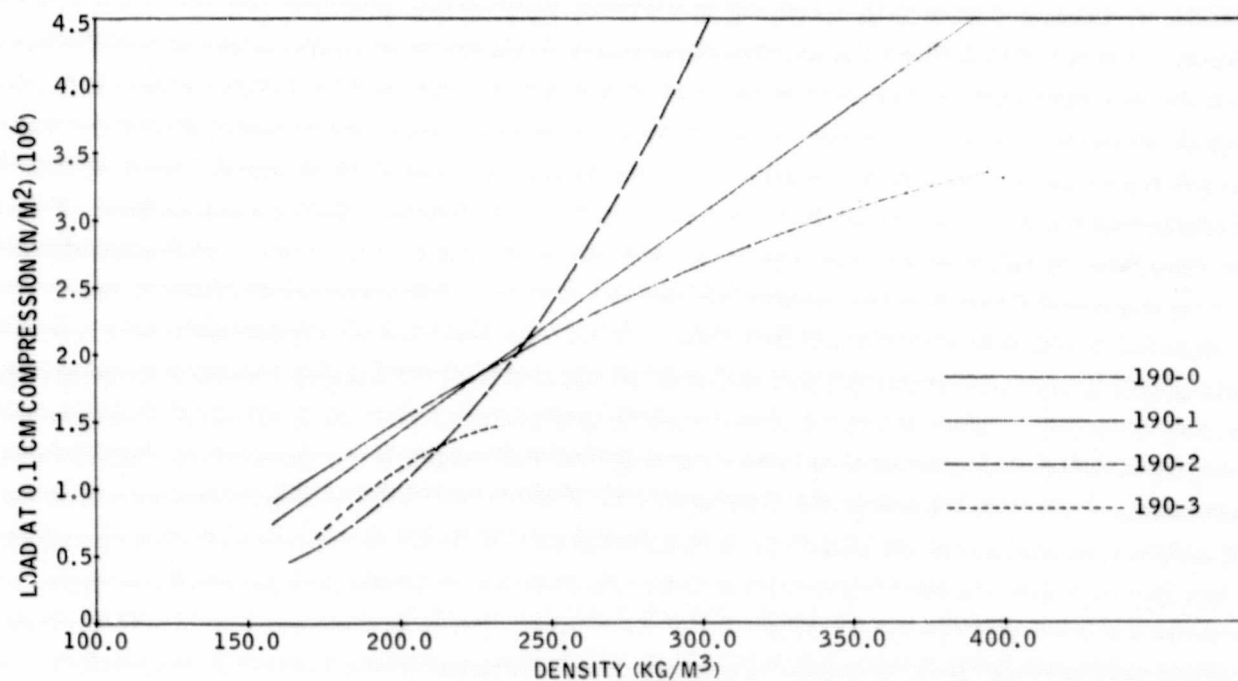


Figure 40. Compressive Strength of 190 Series Resins Filled With Chopped Carbon Mat

strength-density curves which tends to fall off at higher densities. Resin 190-2 shows a reasonably favorable curve although it did not consistently yield the highest strength relative to the others. Resin 190-2 was the only candidate selected from this series.

On the basis of these preliminary screenings, the following resins were selected for further study:

- E-160-3
- E-160-5
- E-170-2
- E-170-3
- E-190-2

(2) Evaluation of Reinforcements

After selection of the candidate resins, attention was shifted to evaluation and screening of reinforcements by determination of their contributions to the mechanical properties of the systems. The reinforcements selected for this study were the following:

Carbon Mat, single layer, approximately 2.5 cm (1 in.) thick. VMA Grade Union Carbide Corp.

Chopped Carbon Mat, 1.25 cm (0.5 in.) size, VMC Grade, Union Carbide Corp.

Graphite Fiber, 0.62 cm long (0.25 in.), WFA Grade, Union Carbide Corp.

Carbon Fiber, 1.25 cm long (0.5 in.), VFA Grade, Union Carbide Corp.

Fiberfrax, Carborundum Co.

Nomex Fiber, 2.5 cm long (1 in.), Dupont

Kevlar Fiber, 5 cm long (2 in.), Dupont

Chopped glass strands, 832 Binder, 1.25 cm long (0.5 in.), Thalco Glass Fibers Products

The most promising resin candidate from each of the three series was used in the evaluation of each of the fillers listed above. The results of these studies are shown in Figures 41, 42, 43, and 44. Curves for the chopped glass strands are not reported here, since in the early phase of this study, this filler was found to be incompatible with the polyimide resins. These difficulties were later overcome as it will be reported in the sub-section dealing with new configurations.

In almost every case the contribution of chopped carbon mat to the compressive strength of the panels was significantly more pronounced than

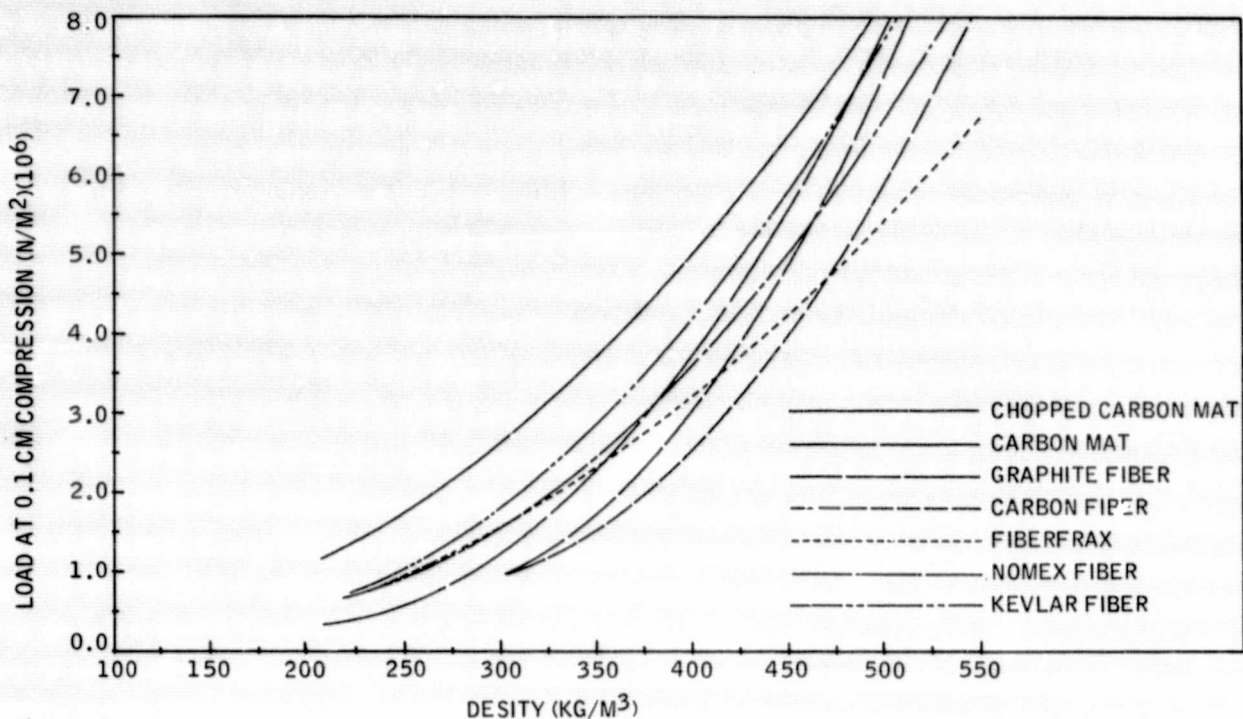


Figure 41. Compressive Strength of 170-2 Resins Filled With Various Reinforcements

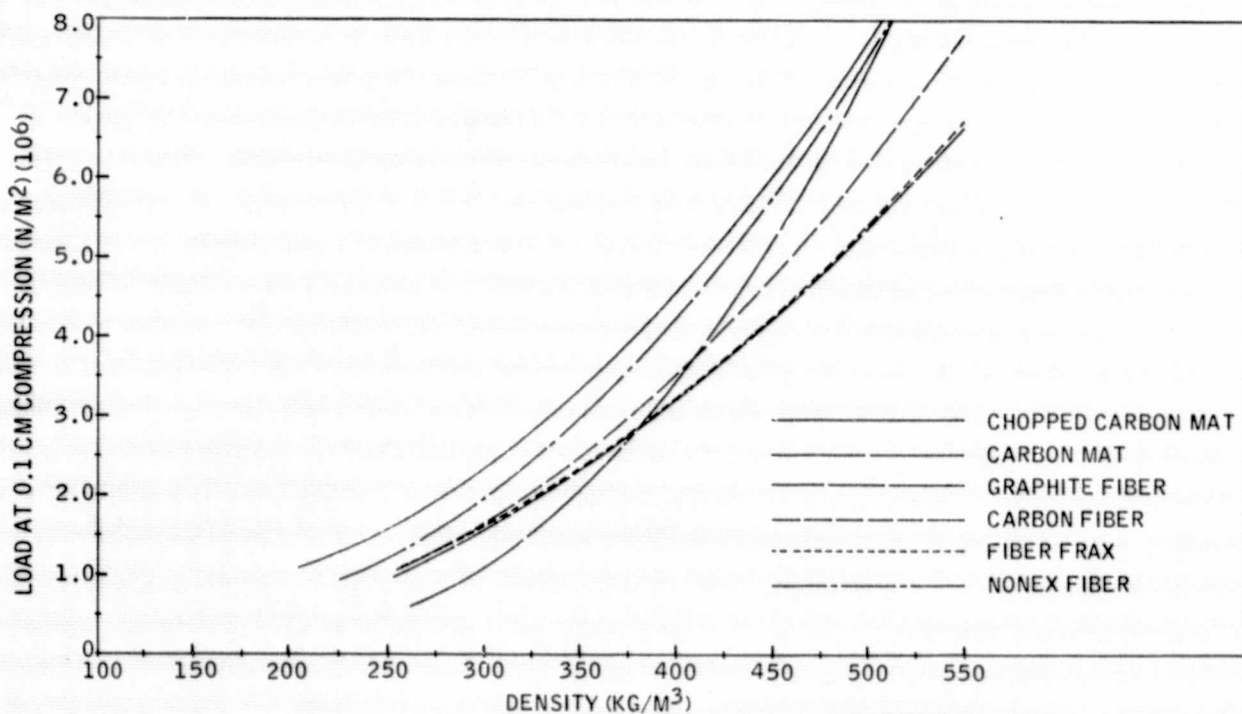


Figure 42. Compressive Strength of 170-3 Resins Filled With Various Reinforcements

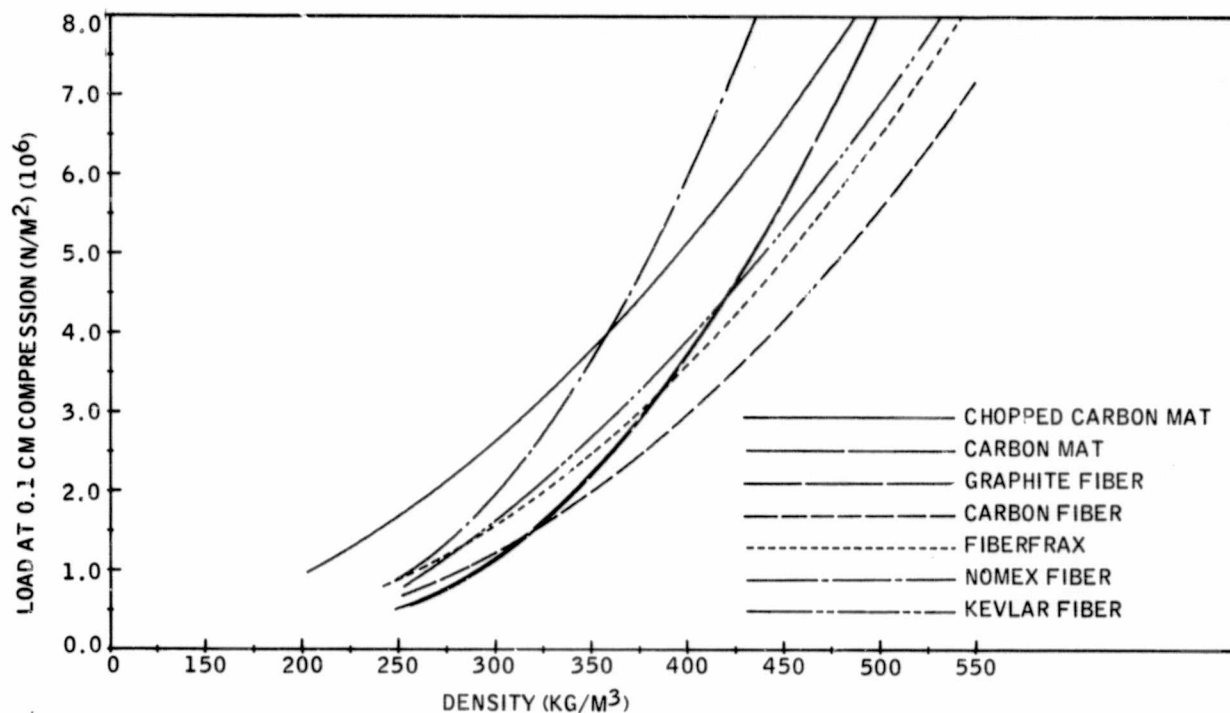


Figure 43. Compressive Strength of 160-3 Resins Filled With Various Reinforcements

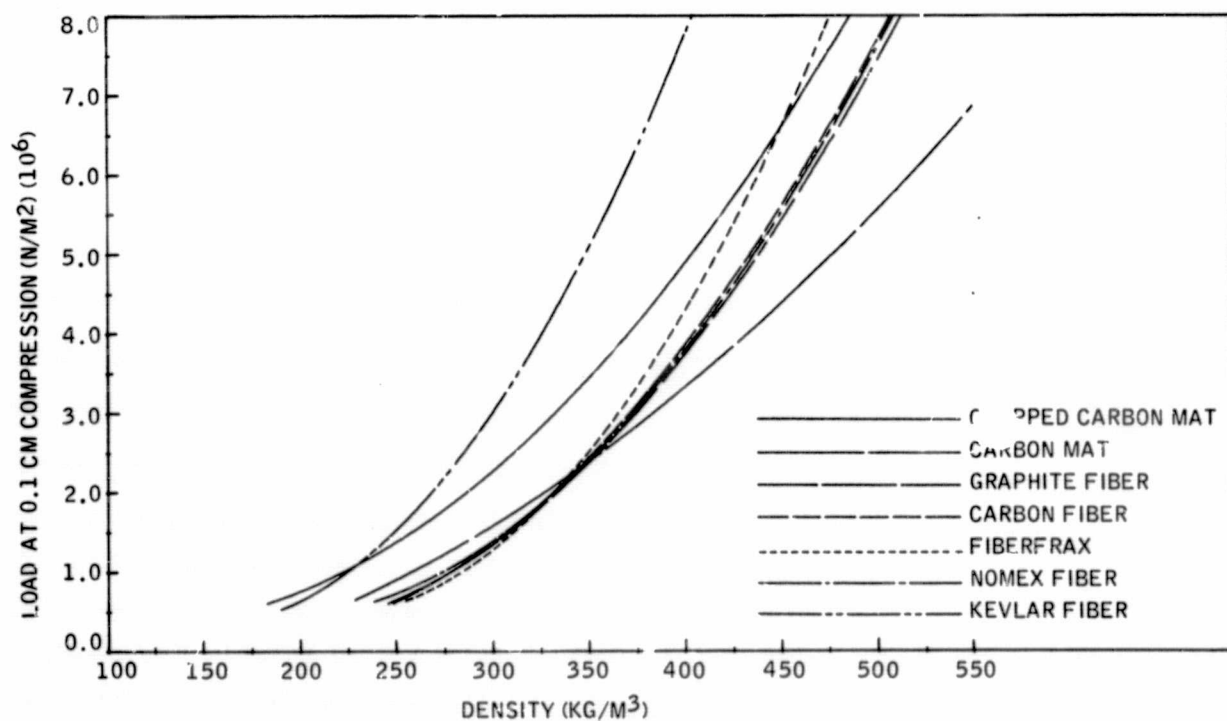


Figure 44. Compressive Strength of 190-2 Resins Filled With Various Reinforcements

with any other filler evaluated in this phase of the program. Other fillers that exhibited good results were Nomex and Kevlar fibers. This is shown in Figures 42 and 43 for Nomex-170-3 and Nomex-160-3 systems and in Figures 41 and 44 for Kevlar-170-2 and Kevlar-190-2 systems.

Single layers of carbon mat did not show the level of contribution we had expected, however, rigid panels made from continuous mat possessed the most uniform foam structure with the best surface finish. On the basis of this study the fillers selected for further optimization of polyimide rigid panels are the following:

Carbon mat, single layer 2.5 cm (1 in.) thick

Chopped carbon mat, 1.25 cm (0.5 in.) size

Nomex fibers, 2.5 cm (1 in.) long

Kevlar fibers, 5.0 cm (2 in.) long

After this preliminary screening, a study was initiated to optimize the rigid panels by evaluation of the effect of fiber length, filler concentration and system loading.

The investigation of the effect of fiber length on the strength-density relationship, was carried out by fabrication of panels made with graphite fiber having lengths of 1.25 cm (0.5 in.), 0.625 cm (0.25 in.) and 0.312 cm (1/8 in.). The data obtained from testing showed no significant contribution of fiber length to the compressive strength of the rigid panels.

The study was continued with the effect of concentration of the reinforcement on the strength of the rigid panels. Test samples were made with three candidate fillers; carbon mat, chopped carbon mat and Nomex fibers using E-160-5 liquid polyimide precursor. For each of the fillers six samples were made at a filler concentration of 2.5, 5.3, 7.9, 10.6, 13.2 and 15.9 percent based on polyimide solids. This range of concentration was selected based on preliminary observations of the mechanical properties of the systems. Above 16 percent concentration the fibers were poorly wetted and the system became resin starved; below 2 percent there was insufficient filler to provide strength to the system. This data is shown in Figure 45 and was obtained by polynomial fitting data points representing specific strength (compressive strength/density) at various filler concentrations. The curves show that the optimum filler concentration is in the area of 8-16 percent. This study also showed that by varying the filler concentration, the rise of the foam also varied. Specifically panels with a lower filler concentration give higher foam rise for concentrations above 4 percent. Below this level the rise tended to level off. This characteristic proved significant in the development of the low density wall panels as discussed later.

Finally, a study was initiated to evaluate the effect of loading on panel strength. This was done by varying the amount of the resin/filler composition per unit area. Samples were made using E-160-5 liquid precursor filled with chopped carbon mat at a concentration of 10.6 percent based on polyimide solids. The following total solid loadings were evaluated:

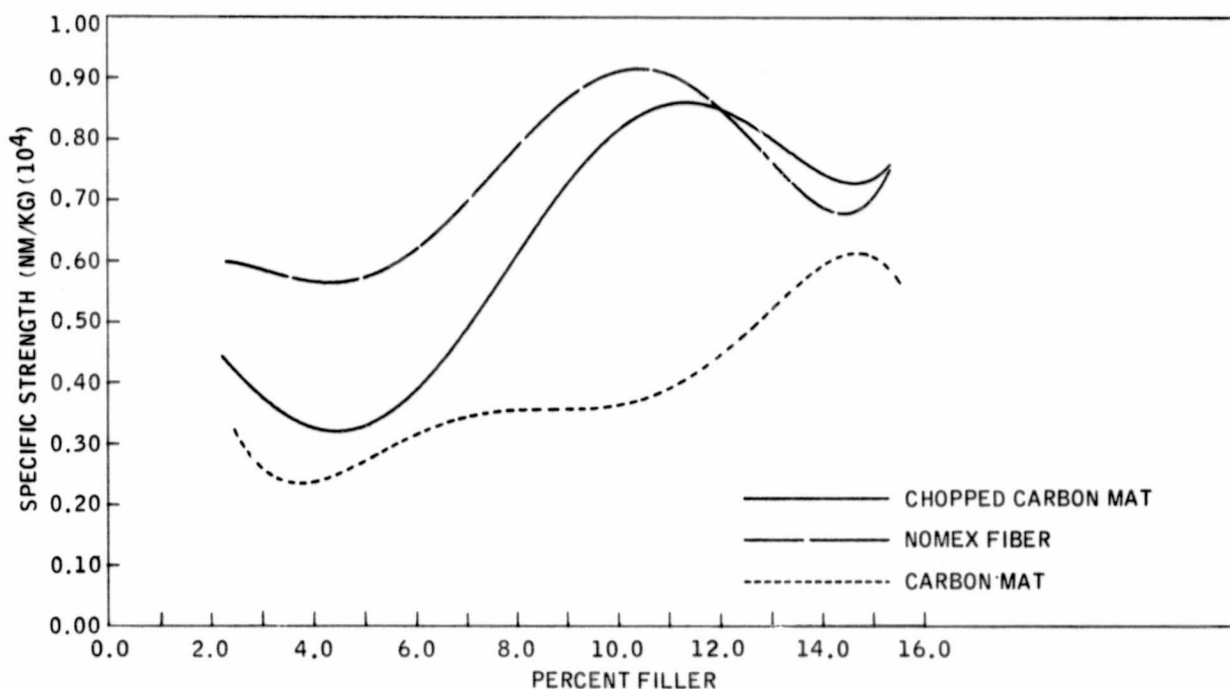


Figure 45. Filler Concentration; Effect on Compressive Strength of 160-5 Filled Resins

0.425 g/cm²
 0.305 g/cm²
 0.229 g/cm²
 0.178 g/cm²

The results of these tests are shown in Figure 46. The data shows that, within this range, loading has no significant effect on the compressive strength of the system, since the curves tend to follow the same distinct strength-density relationship. This indicates that rigid panels produced by this process possess strength characteristics which are almost entirely a function of the density.

(3) New Configurations, Foam Filled Honeycomb

In an effort to improve the most critical properties of the rigid panels, several new configurations were studied. The most direct contribution to strength was obtained by filling a honeycomb with a polyimide foam. In addition, attempts were made to improve the compressive strength of the panels with a series of mechanical reinforcing mechanisms and by the use of chopped glass strands.

The honeycombs used in this study were type HRH-327 and HRH-10, purchased from the Hexcel Corp. in a variety of cell size and thickness. The honeycombs meet the specifications for compressive strength and bending

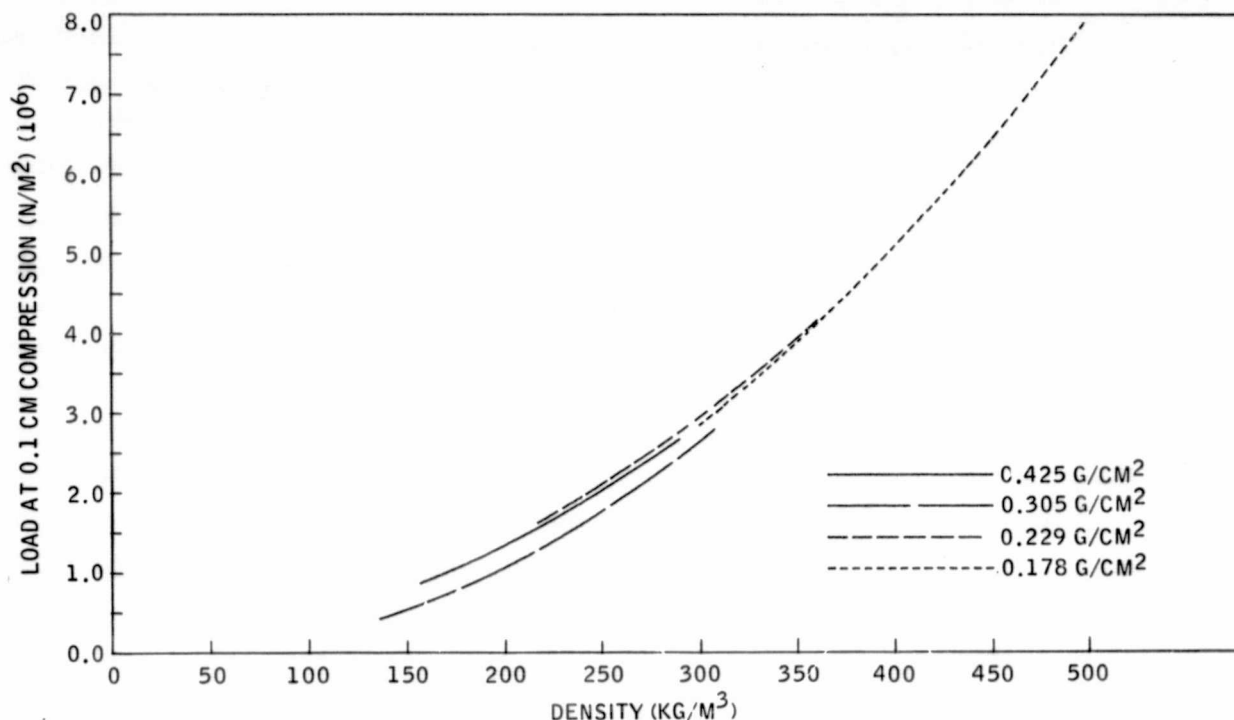


Figure 46. Effect of Loading on Compressive Strength of 160-5 Filled Resins

strength in their original state. To give these panels the desired thermal properties the cells were filled with a low density polyimide foam using the resins of system 160 and 170 by the process reported in Section 3.5. The foam added to panel rigidity while increasing density only minimally. To improve cell wetting during the dipping procedure and also to attempt to improve the fire hardening characteristics of the foam, certain fillers were added to the resin, specifically micron size carbon fiber and graphite powder. Flame tests carried out using a Meker burner showed improved resistance to flame impingement erosion for honeycomb structures filled with 90 percent polyimide solids/10 percent graphite foam compositions with only small density increases over systems without graphite. Figure 47 shows both filled and unfilled samples of large and small cell honeycombs; Figure 48 shows a single larger panel. This process was scaled-up for production of large size honeycomb panels, 55 x 85 cm (22 x 36 in.), for evaluation in a NASA-LBJ Space Center funded program carried out by the Boeing Company, contract NASA9-15062.

Several structural approaches were also taken to improve the strength-density relationship of regular compressed foam panels. Figure 49 shows a high density panel which was lightened by cavities spaced in a pattern to minimize loss in panel flexural strength and at the same time reduce panel weight. The burn characteristic of this panel was marginal and the concept abandoned. Figure 50 shows a panel produced by using a high density grid from resin impregnated Nomex fibers. The spaces in between the grid were filled with low density polyimide foam. The compressive strength of this panel was 3.31×10^6 N/m² (480 psi) at density of 308 kg/m³ (19 lbs/ft³). The burn

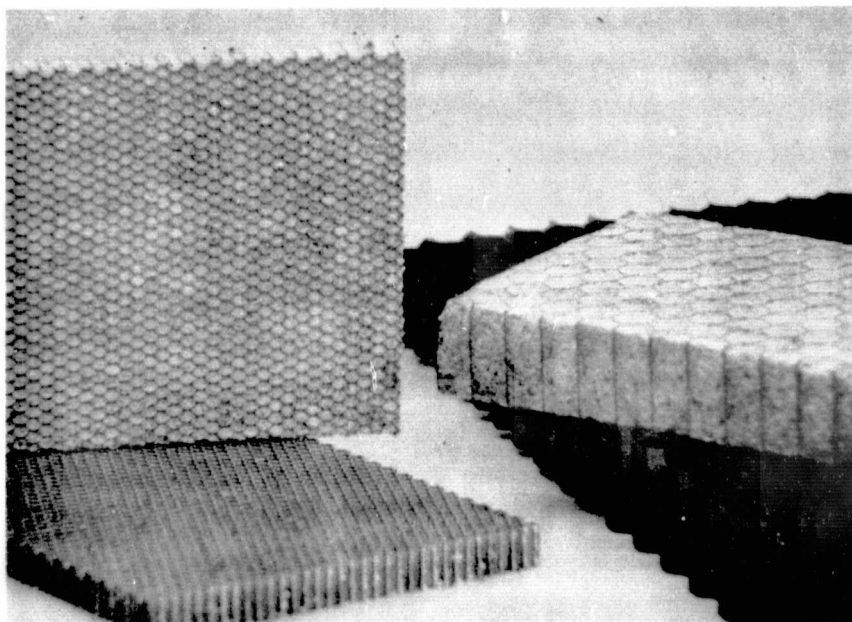


Figure 47. Polyimide Foam Filled Honeycomb

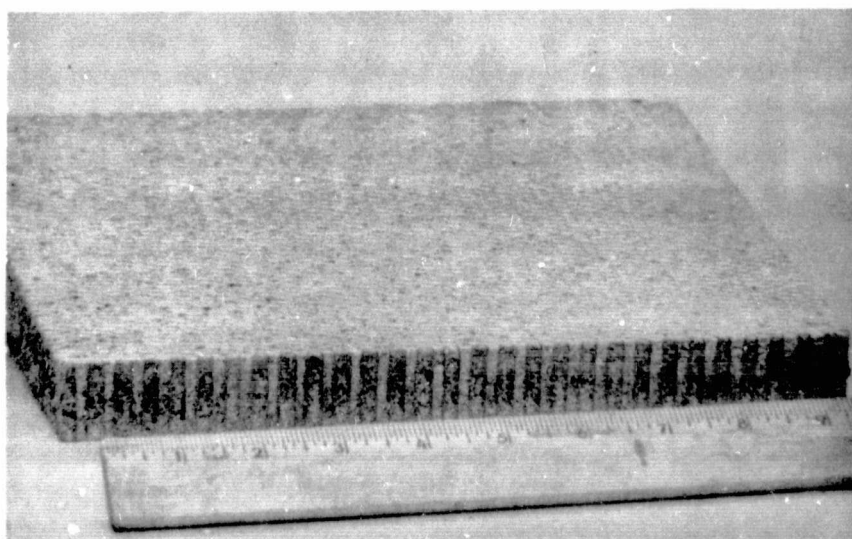


Figure 48. Polyimide Foam Filled Honeycomb

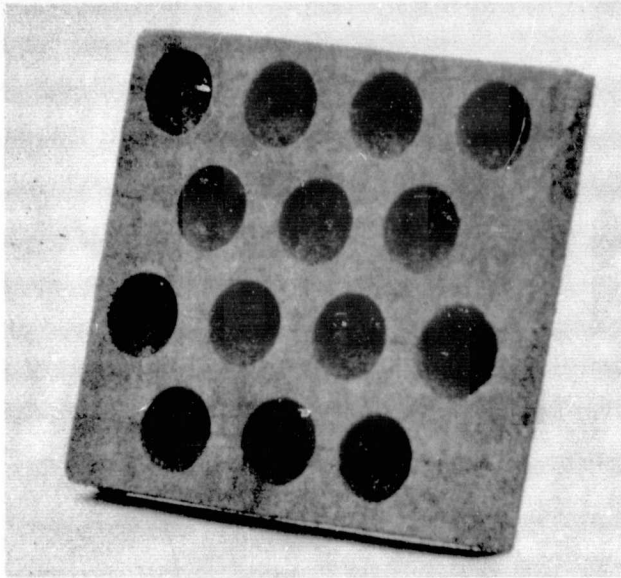
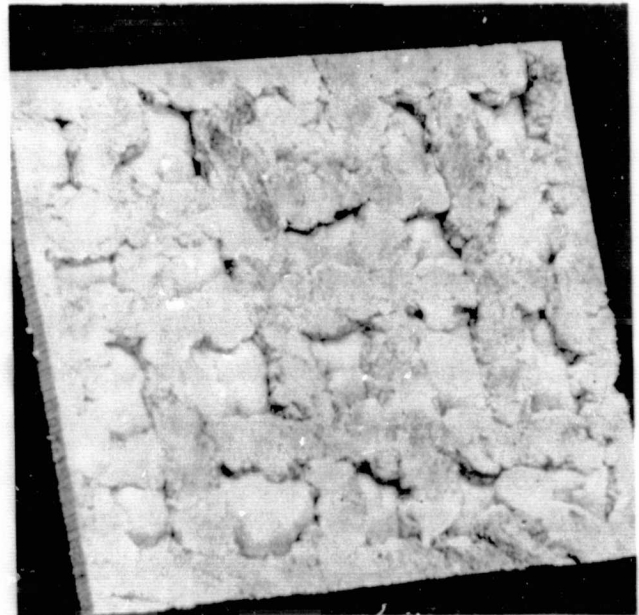


Figure 49.

Polyimide Rigid Panel - New Configuration

Figure 50.

Polyimide Rigid Panel - New Configuration



characteristics of the panel met the requirements, but the density was too high. Figure 51 shows three samples cut from a panel fabricated with vertical reinforcing strips produced by impregnating asbestos fabric with a polyimide resin. The compressive strength of this configuration was $4.82 \times 10^6 \text{ N/m}^2$ (700 psi) at a density of 251 kg/m^3 (15.5 lbs/ft³).

These approaches appeared to be feasible but had deficiencies in certain areas. It was not within the scope of this program to attempt the optimization of all these new concepts; only those which appeared to offer specific advantages were further investigated. One of these was chopped glass strands filled systems.

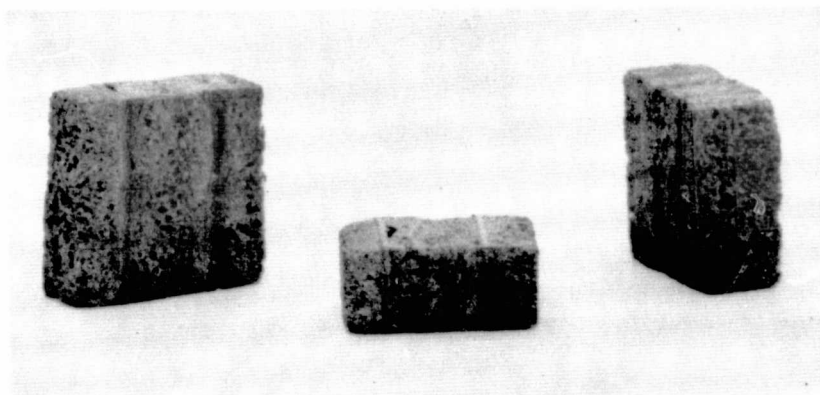


Figure 51.

Polyimide Rigid Panel -
New Configuration

The use of glass fibers in polyimide foams was attempted in previous studies carried out at Solar, but soon abandoned due to incompatibility of the glass fibers with the foaming process. This resulted in low foam rise and brittle foam structure. Improved results were obtained when chopped glass strands with 832 binder were used.

A series of experiments was initiated to delineate the process parameters for fabrication of glass filled rigid panels. The previous work carried out with chopped carbon mat had shown that liquid resin precursor 170-2 modified with 1% FC-430 was the strongest resin/surfactant combination. Therefore, this system was used for the glass fiber studies. A loading rate of 1.25 g solids/in.² was selected to return a panel density of under 192 kg/m³ (12 lbs/ft³) at 1.0 cm (0.40 in.) thickness.

The first step was to determine the optimum chopped glass strands concentration to give both good strength and sufficient rise for a smooth panel surface. Table XXIII shows the results of this study. The 15 percent glass concentration was found to give best results for the intended use.

It was determined earlier that the B-staging temperature has a significant effect on foam rise, strength and hardness of the rigid panels, therefore the glass filled compositions were again tested over a complete range of temperatures from 76.7°C (170°F) to 93.3°C (200°F). At a drying temperature of 85°C (185°F) the foam showed good cellular structure and sufficient rise to yield smooth surfaces when compressed to 1.0 cm (0.4 in.). Fiber lengths of 0.625 cm (1/4 in.) and 1.25 (1/2 in.) were studied with no significant differences. The best strength obtained with chopped glass strands was 2.41×10^6 N/m² (350 psi) at 184 kg/m³ (11.5 lbs/ft³) using a glass concentration of 15 percent based on polyimide solids and a B-staging temperature of 85-87.7°C (185-190°F). This composition and process was later scaled-up for fabrication of an additional candidate floor panel selected on the basis of quality and low cost.

On the basis of the data reported, two resins were selected as candidates for additional studies of optimization. These resins were E-160-5 and E-170-2. In addition, four reinforcements were screened for studies in conjunction with the two resins. These were single layer carbon mat, Nomex fibers,

Table XXIII
Rigid Panels; Effect of Glass Strands Concentration on Properties

Percent Filler	Foam Rise		Panel Surface Quality	Compressive Strength N/m ²
	cm	inch		
10	1.5-2.0	0.6-0.8	No surface imperfections	1.18×10^6 at 192 kg/m ³
15	1.25-1.5	0.5-0.6	Few surface imperfections	1.7×10^6 at 165 kg/m ³
20	1.0-1.25	0.4-0.6	Heavy surface imperfections	2.31×10^6 at 212 kg/m ³
25	1.0	0.4	Rise too low for rigid panel use	---

chopped carbon mat and chopped glass strands. The panel configurations selected were the compressed polyimide foam panels and the foam filled honeycomb structures. These were further optimized as will be discussed next.

4.2.3 Process Parameters/Panel Configuration

The effort of this task is focused on optimization of process parameters and development of advanced compositions to produce rigid panels meeting specific requirements. This work has been organized in such an order as to provide data on the most critical parameters in the early phase of the effort and proceeds in the sequence (1) evaluation of surface active agents, (2) evaluation of reactive additives, (3) optimization of process parameters, (4) investigation of substrate materials, and (5) selection of candidates.

(1) Evaluation of Surface Active Agents

This phase of the program involves the use of surface active agents to improve the wetting characteristics of the resins for a better interaction of the resin/filler system. In the first phase of this study an array of 12 different surfactants was tested using resin E-160-5 filled with chopped carbon mat at 8 percent concentration based on polyimide solids. All test samples were fabricated at the same surfactant concentration (0.5 percent based on polyimide solids) and under the same process conditions. The effect of the surfactant was evident for several of the systems while other surfactants adversely affected the strength of the rigid panels. Figure 52 shows the effect of six selected surfactants on the compressive strength of the rigid panels. These surfactants were: L-530, L-5420, L-5430, L-5410, FC-430 and FC-431. Generally the contribution of surface active agents on

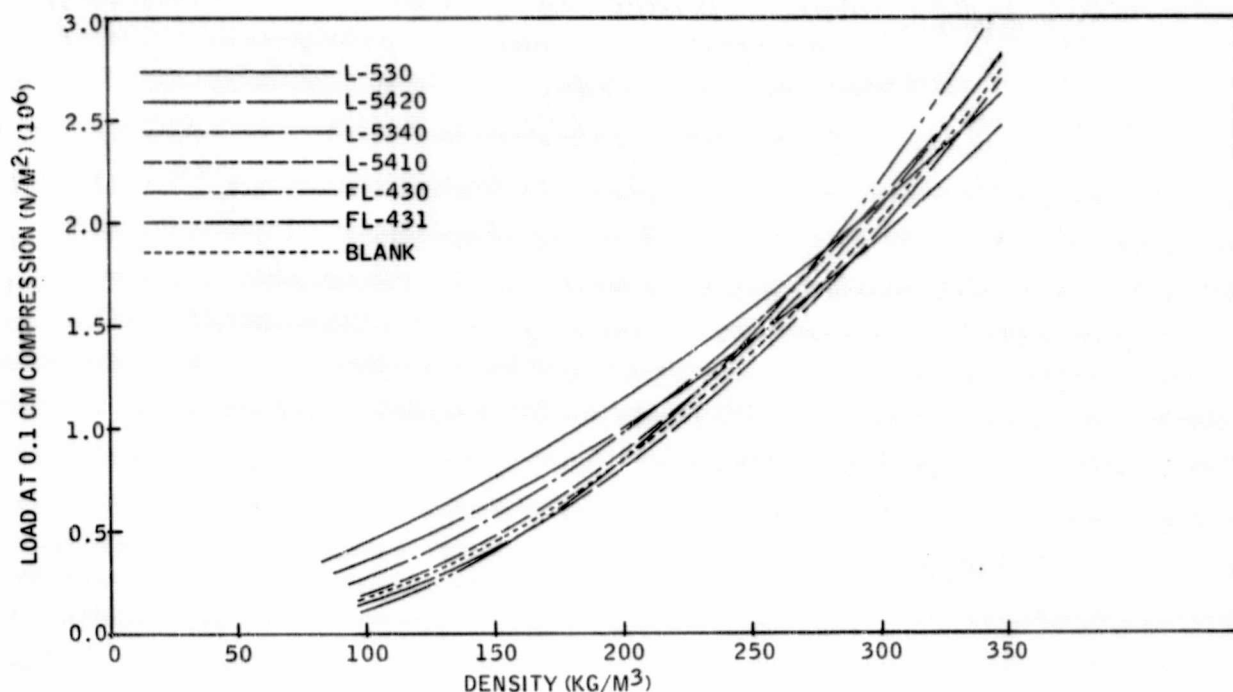


Figure 52. Surfactants, Effect on Compressive Strength of 160-5 Filled Resins

strength was more evident in the low density region as it is shown next. Figure 53 shows test data obtained with four surfactants, L-530, L-5340, L-5410 and FC-431 (0.5 percent concentration based on polyimide solids) with resin E-170-2 filled with 8 percent chopped carbon mat. In this system L-530 showed the most significant effect on the strength of the material. As a result of this study the following surface agents were selected for further evaluation. These are: L-530, L-5420, FC-430 and FC-431. The lowest density foam and highest rise were produced by the use of resins modified with FC-431.

(2) Evaluation of Reactive Additives

L-170 and L-169, two fluorocarbons evaluated as additive in the study dealing with flexible resilient foams were also evaluated for their effect on the strength of rigid polyimide foam panels. A series of experiments were carried out using resin 160-5 filled with chopped carbon mat at a concentration of 8 percent based on polyimide solids. L-170 was added to the liquid resin at various concentrations. Figure 54 shows the compressive strength of the rigid foams at increasing concentration of L-170. The data shows that the addition of L-170 improves the strength-density relationship of rigid panels, however, the degree of improvement varies with no particular correlation to the level of the additive. Although the results obtained did not warrant additional effort, it was noticed that the foams modified with

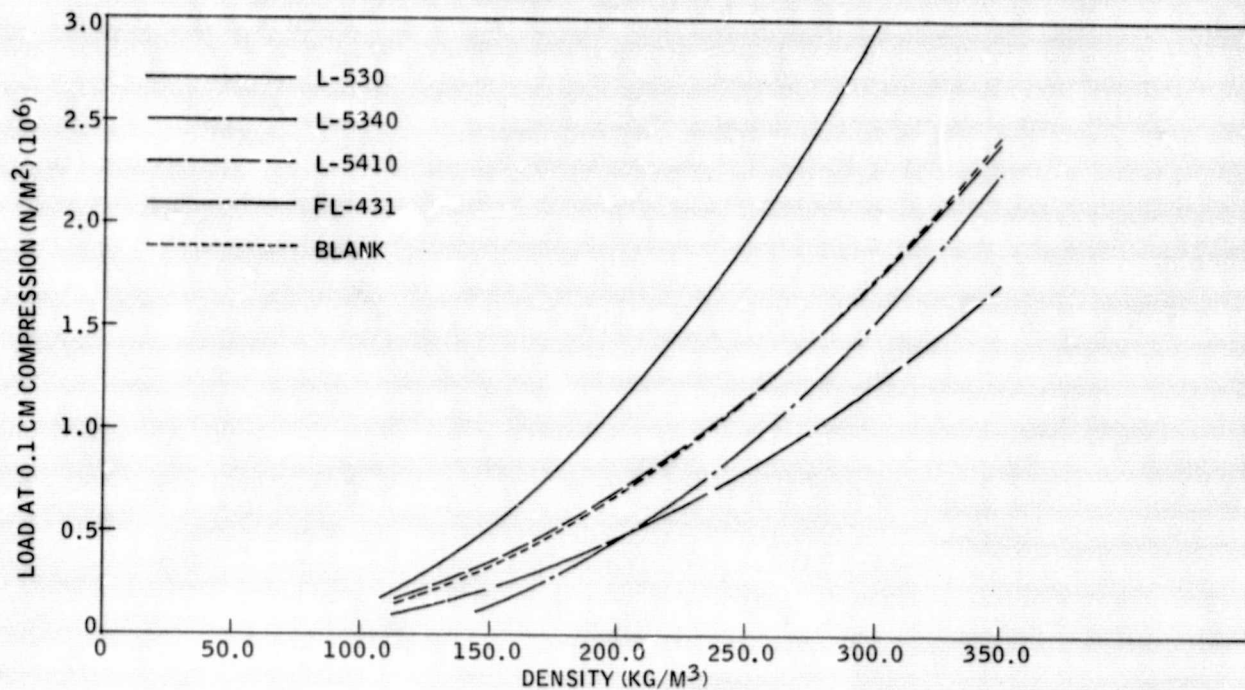


Figure 53. Surfactants, Effect on Compressive Strength of 170-2 Filled Resins

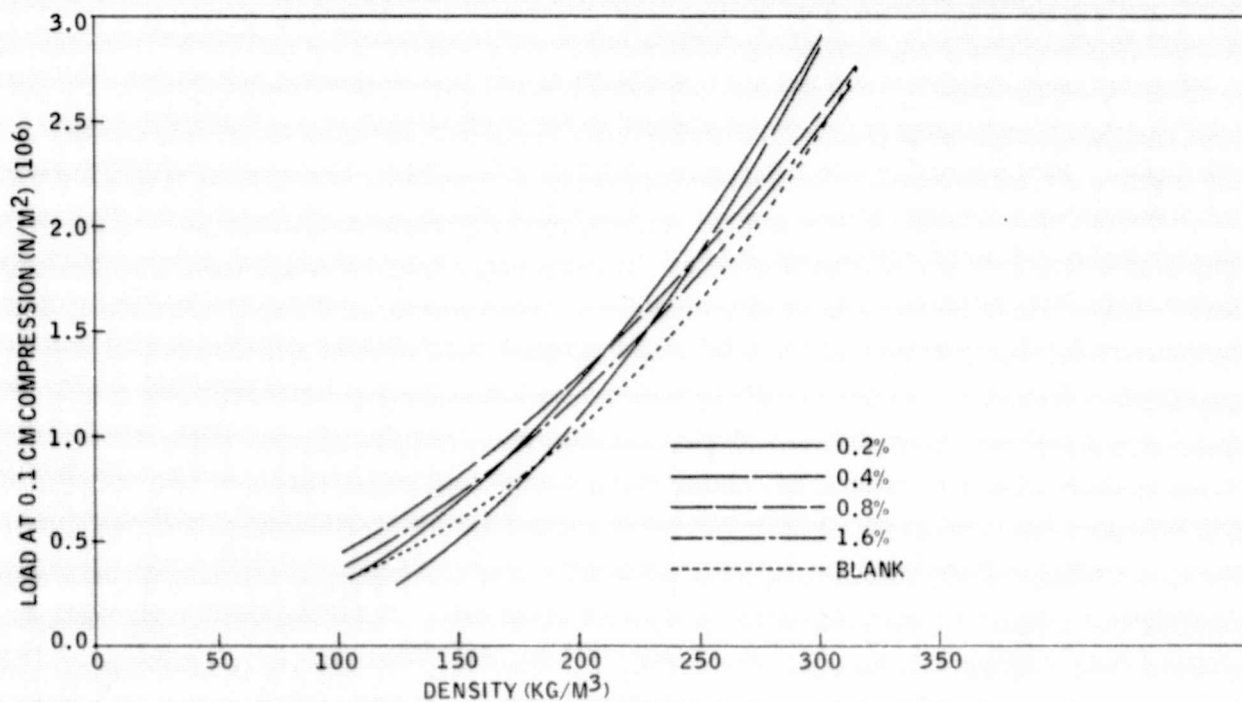


Figure 54. L-170 Additive, Effect on Compressive Strength of 160-5 Filled Resins

L-170 were characterized by a hard, dense skin and a low density core. This behavior was more evident with panels prepared from the powder precursor. It is important to capitalize this technology by further optimizing the system in a continuation program and developing it into a stage ready for large panel production. Immediate results will be the production of rigid foams possessing dense hard skin and low density core ready to be fabricated into finished wall panels by lamination of decorative skins.

(3) Process Parameters

This phase covers the optimization of process parameters and includes studies of distribution of fillers, evaluation of the B-staging temperature, and synergistic effects to achieve optimum mechanical properties.

The study to improve the distribution of the reinforcements in the liquid precursors was done using a mechanical Kitchen Aid mixer model K-5A. The procedure consisted of adding the desired surface active agent (FC-430 at concentration of 1.0%) to the 170-2 resin followed by mixing the mixture at a speed of approximately 200 RPM for 2 minutes. This was followed by adding the chopped carbon mat over a period of three to five minutes and the mixture mixed for an additional 5 to 10 minutes. A control sample was prepared in the usual manner by hand mixing for 3 to 4 minutes until the mixture was homogeneous. All panels were dried at B-staging temperature of 82°C (180°F). It was observed that mechanical mixing resulted in breaking down the carbon mat chunks to individual fibers, causing an apparent increase of viscosity and an increase of volume due to the amount of air trapped into the viscous mixture. These compositions were easily applied in a uniform manner and produced foam panels with improved surface characteristics and significantly more uniform structure throughout. In general, the longer the mixing period the higher the rise of the polyimide foam, however, this also resulted in a decrease of the compressive strength as shown in Figure 55. The decrease of strength is most probably due to the breaking down of the carbon mat chunks which had provided the mechanism for strength in compression. The final process for compounding chopped carbon mat was improved by using a low speed paddle mixer which produced low shearing of the viscous mass and prevented breaking down of the carbon fibers. Although chopped glass strands did not break under the effect of shearing, the same process was also used for this type of reinforcement.

The study of the effect of the B-staging temperature on the mechanical properties of the rigid panels was carried out by preparing samples with candidate resin E-170-2 filled with 8 percent chopped carbon mat followed by B-staging at 60°C (140°F), 71°C (160°F), and 82°C (180°F). The rigid foamed samples made at these different conditions showed marked differences. The foam rise was found to be a function of the drying temperature, the higher the drying temperature the lower the foam rise and the higher the density of the rigid panels. The strength-density relationship of the specimens processed at the above conditions is shown in Figure 56. The rise of the foam B-staged at 82°C (180°F) was only sufficient to give a reasonable surface when the panel was compressed to a thickness of 1 cm (0.4 inch) and

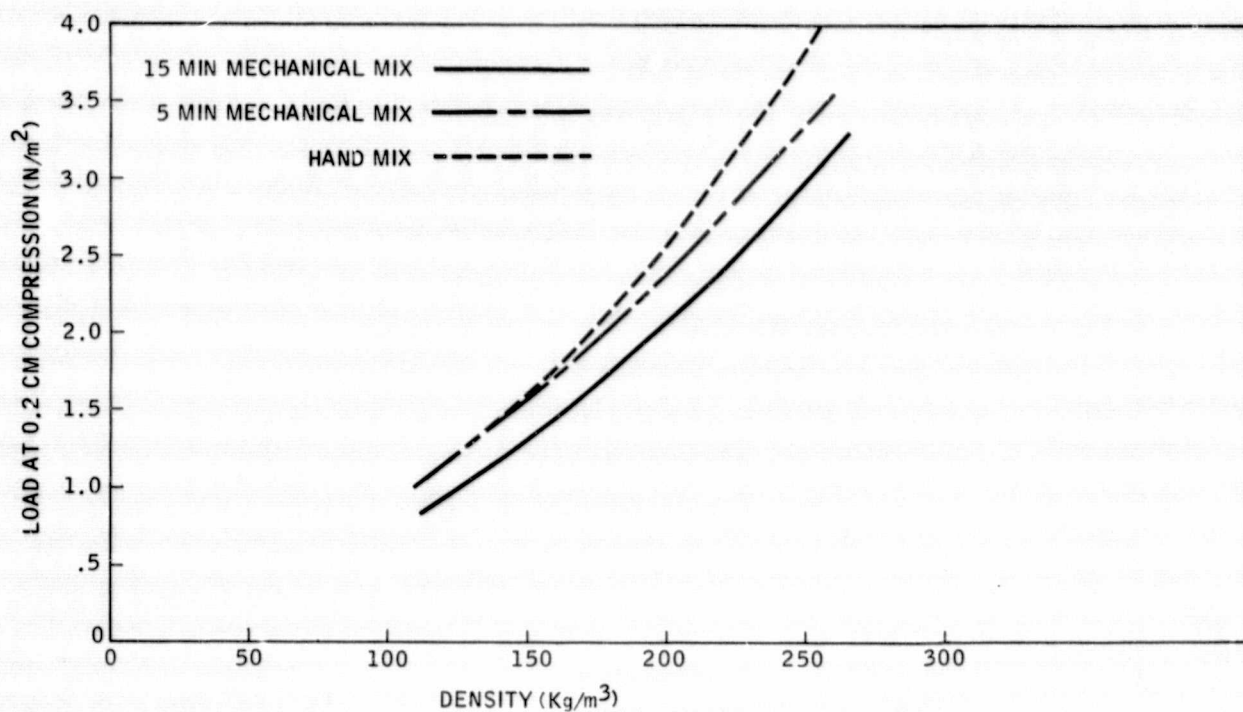


Figure 55. Processing Parameter; Effect on Compressive Strength of Rigid Panels (170-2)

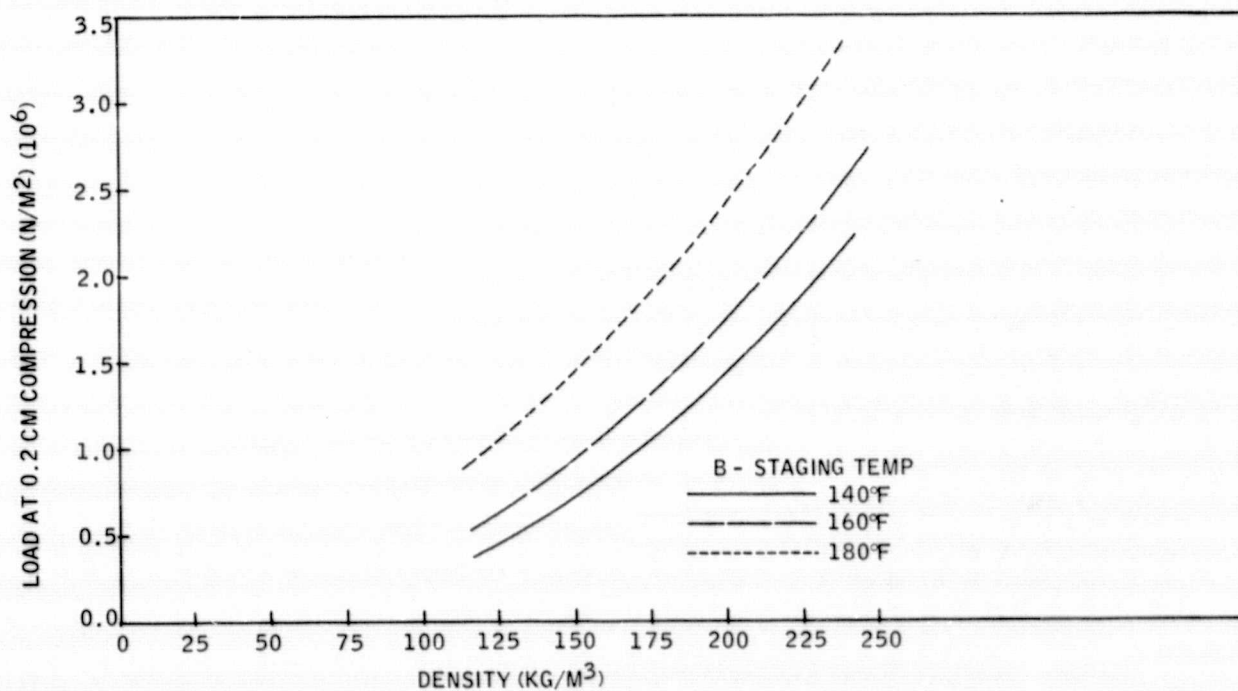


Figure 56. Drying Temperature; Effect on Compressive Strength of Rigid Panels (170-2)

the compressive strength of the panel reached a value of approximately 2×10^6 N/m² (300 psi). This was below a strength of 3.4×10^6 N/m² (500 psi) required for floor panel applications.

Next the three parameters: reactive agents, surfactants and drying temperatures were combined in a comprehensive study to determine synergistic effects on strength. Panels were made from 170-2 chopped carbon mat filled compositions with the following additions:

1. Control
2. 0.8% L-170 reactive agent only
3. 1.0% L-530 surface active agent only
4. 0.8% L-170 + 1.0% L-530

All percentages were based on polyimide solids. The compositions were dried at a B-staging temperature of 82°C (180°F) and foamed according to the process reported in Section 3.5. The results of these tests are shown in Figure 57 and are summarized as follows:

The addition of surface active agent L-530 alone produced rigid panels with the most improved strength-density relationship (3.4×10^6 N/m² at 220 kg/m³, 500 psi at 13.5 lbs/ft³).

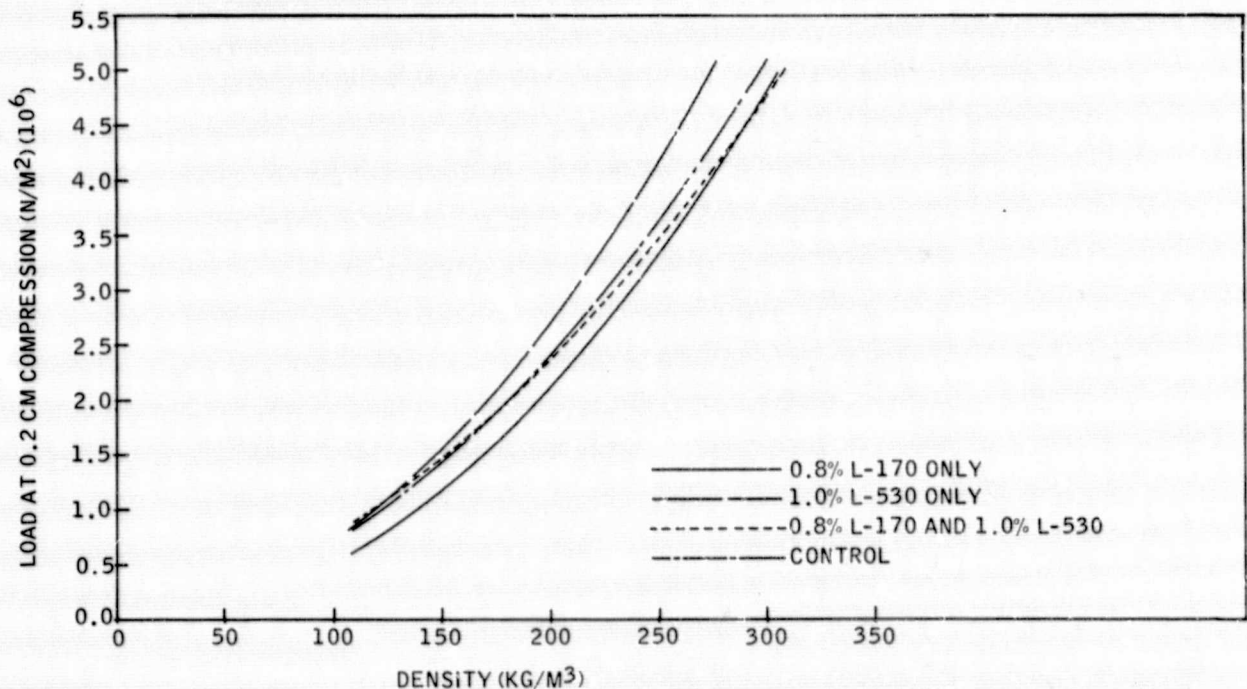


Figure 57. Resin Additions; Effect on Compressive Strength of Rigid Panels (170-2)

The addition of reactive agent L-170 decreased the compressive strength of the rigid panels and reduced the effectiveness of L-530 when used in conjunction with that surfactant.

Rigid panels produced with L-530 met the compressive strength value of $3.4 \times 10^6 \text{ N/m}^2$, which was established as a goal for this program but the panel density was higher than that recommended.

At the conclusion of this study we were advised by Union Carbide that L-530, the selected surface active agent for the rigid panels, was not available any longer. No reasons were given. Substitute surfactants were recommended by Union Carbide, but did not produce the desired results. This study of optimization was continued with evaluation of other candidate surface active agents to select final compositions for fabrication of test specimens for submittal to the Boeing Co. These surfactants were L-5420 and FC-430. Comparative studies were therefore carried out and FC-430 was selected for its characteristics to produce a higher foam rise, more uniform structure and higher strength characteristics than those obtained with L-5420.

Additional investigations were carried out to determine the effect of surfactant concentration. This study was done using resin E-170-2 modified with FC-430 using chopped carbon mat reinforcement. Four small-scale panels were made with the following FC-430 concentrations based on polyimide solids - 0%, 0.5%, 1.0%, and 2.0%. Results of this study are given in Table XXIV. All panels were fabricated at a density of 192 kg/m^3 (12 lbs/ft^3).

Table XXIV
FC-430 Surface Active Agent Concentration; Effect on
Compressive Strength (E 170-2)

FC-430 %	Foam Rise		Panel Surface Quality	Compressive Strength	
	cm	inch		N/m^2	psi
0	1.52-2.54	0.6-1.0	Very Good	1.6×10^6	233
0.5	1.27-2.04	0.5-0.8	Very Good	1.8×10^6	267
1.0	1.27-2.04	0.5-0.8	Very Good	1.9×10^6	277
2.0	1.01-1.77	0.4-0.7	Very Good	1.9×10^6	283

The data shows that panel strength increases with increased surfactant concentration within the tested range. However, this is accompanied by a decrease in initial foam rise. The foam rise is a very important parameter because it affects the surface quality of the panel leaving an inadequate area for bonding the final skins. In these small samples the foam rise was

sufficiently high in all cases, however in larger scaled-up samples the foaming behavior was found to be erratic and to result in non uniform surfaces. For this reason the lower concentrations of surfactant were found to be advantageous in fabrication of floor panels. The optimum concentration of FC-430 was selected to be in the range of 0.5%. This data became available during the last phase of the program, hence these improved conditions were only used to prepare the final samples for submittal to NASA-LBJ Space Center.

Screening and selection of the optimum process parameters and panel configurations were carried out by determination of the compressive strength of the final rigid panels. The test was carried out in accordance with the procedure described in Section 3.5 which is an ASTM method recommended for testing honeycomb structures. The compressive strength of the materials was taken as the maximum load value within 0.1 cm (0.04 in.) strain since at higher strain values the honeycomb structure show permanent deformation. The polyimide rigid foams, however, have shown an elastic recovery of 85-100 percent without damage to cell structure when compressed at strain levels as high as 0.3 cm (0.12 in.). A change of procedure was recommended and incorporated in the testing program. This change permits taking the compressive strength of the rigid panels at a maximum load value within 0.2 cm (0.08 in.) strain.

(4) Investigation of Substrate Materials

This effort was undertaken to study processes for fabrication of rigid panels by foaming a polyimide resin directly on suitable substrates to achieve foaming and skin lamination in a single step.

The substrates evaluated in this task were those reported in Section 4.5, dealing with optimization of polyimide coated fabrics. These included:

- Style 181 glass fabric
- Style 120 glass fabric
- Style 28 P067N Asbestos cloth
- Nomex paper 0.5 mm (2 mil) thick
- Nomex paper 2.5 mm (10 mil) thick

Foaming and lamination were accomplished by spreading out the resin-filler composition on the fabrics followed by B-staging and foaming. The panels were then compressed to the desired thickness in a platen press at 287.7°C (550°F).

The fabrics exhibited good shape retention during the foaming and compression process with the exception of 0.5 mil Nomex and 120 style glass fabric. Fabric adhesion to the foam core was 523.3 N/m (3 lbs/in.) maximum when tested at 90 degree angle; in all cases the fabric broke by brittle failure.

This deficiency was overcome by modification of the process used in the preparation of the coated fabrics. This was accomplished by curing the fabric at a temperature in the range of 204-237°C (400-450°F). This development will be more succinctly discussed in Section 4.5 which covers the screening and selection of fabrics and coating processes. The lower curing temperature improved the tear resistance of the glass fabric, however the bond strength did not improve and failure occurred by tear of the foam core. Simultaneous foaming and lamination techniques may have potential if this process is further optimized in a continuation of the program to develop it into a stage ready for larger scale manufacturing. Lacking such a process the skin lamination of the floor paneling developed in this program was done using aircraft unidirectional glass phenolic laminates and it was carried out by the Boeing Co. as it will be discussed in Section 4.2.4.

(5) Selection of Candidates

On the basis of test data and product evaluation the following panel configuration and candidate materials were selected.

i. Panel Configurations

Compressed polyimide foam panels

Foam filled honeycombs

ii. Liquid resin precursors

E-170-2

E-160-5

iii. Reinforcements

carbon mat, single layer, 2.5 cm (1 in.) thick; chopped carbon mat 1.25 cm long (0.5 in.), chopped glass strands 1.25 cm long (0.5 in.).

iii. Additives and surface active agents

L-5420 and FC-430

4.2.4 Specimen Preparation and Screening

This task covers the work pertinent to the selection of candidate systems for fabrication of test specimens for submittal to Boeing Co. The Boeing Co. has been funded by NASA-LBJ Space Center to evaluate commercially available and more advanced floor paneling such as those developed within this program.

The two panel configurations selected in the previous section were scaled-up to select final optimized candidate materials and process parameters. The compressed foam configuration was first evaluated. Large specimens 55 x 85 cm (22 x 34 in.) were fabricated with the three reinforcements, carbon mat, chopped carbon mat and, in the later phase of this study, chopped glass strands. For each of the reinforcements two sets of specimens were fabricated, one with E-170-2 and the second with E-160-5, both resins being modified with 1 percent FC-430 based on polyimide solids. The panels were processed as reported in Section 3.5 and evaluated for the following characteristics: ease of spreading, foaming behavior, visible flaws, color, foam rise, compressive strength and cost. A summary of these experiments are reported in Table XXV. Two reinforcements, carbon mat, chopped glass strands and resin E-170-2, were selected as the optimum candidates. Next an evaluation of the effectiveness of surface active agents was carried out by fabricating large panels with the two selected reinforcements and resin 170-2 modified with FC-430 and with L-5420. The surface active agents were tested for their effect on the foaming characteristics and strength of the panels. FC-430 produced rigid panels with the most homogeneous cell structure and rise. Final floor panel candidates were thus selected and were:

E-170-2 modified with FC-430 using carbon mat reinforcement

E-170-2 modified with FC-430 using chopped glass strands
and chopped carbon mat reinforcements

Table XXV
Floor Panels; Selection of Liquid Resin System

Resin Number	Foam Rise cm	Foam Structure	Surface Quality	Compressive Strength at 192 Kg/m ³		Cost Liquid Resin \$/lb
				N/m ²	psi	
E-160-5	1.90	Very uniform	Very smooth	1.4 x 10 ⁶	205	3.22
E-170-2	1.65	Uniform	Smooth	2.0 x 10 ⁶	285	2.35

The polyimide foam filled honeycomb system was evaluated next by preparing large specimens 55 x 85 cm (22 x 34 in.) produced by filling Nomex honeycombs, type HRH-10-1/8-9 manufactured by the Hexcel Corporation. The filling process was carried out using resins 170-2 and 160-5 both in the liquid and powder form. The process utilizing the powder polyimide precursors to fill the cells produced distortion of the Nomex honeycomb and was abandoned without further effort. The liquid precursors were evaluated next. Foam filled honeycomb panels were produced from the liquid precursors E-170-2 and E-160-5 and examined for filling efficiency, foam rise, cellular structure and density of the final product. Panels produced by filling honeycomb structures with E-160-5 met all the requirements listed above and were selected as the candidate for this application.

The following test panels were then produced having approximate dimensions of 55 x 85 cm (22 x 34 in.) and a thickness of 0.875-1.0 cm (0.39-0.4 in.). The first set of panels were fabricated using carbon mat reinforcement and resin 170-2 modified with 1% FC-430, the second set of six panels were produced by filling Nomex honeycomb type HRH-10-1/8-0 with foams derived from resin E-160-5 without additives, and the third set were made using chopped glass strands reinforcement and resin E-170-2 modified with 1% FC-430. These samples shown in Figure 58(a), (b) and (c) were submitted to the Boeing Co. for testing. During the latest phase of the program, a new set of test panels were fabricated by filling Nomex honeycomb type HRH-1/8-0 with E-170-2 resin filled with 10 percent graphite reinforcement as was discussed in the subsection dealing with new configurations. These panels were also submitted to the Boeing Company for evaluation.

4.2.5 Advanced Testing

The final characterization and testing of candidate materials have been contracted to the Boeing Company under a program funded by NASA-LBJ Space Center.

The compressed foams and foam filled honeycombs are presently being fabricated into finished floor panels by the Boeing Company using protective skins and adhesives meeting aircraft requirements. All physical, mechanical and environmental testings will be carried out in accordance with procedures and specifications adopted for currently used aircraft flooring materials.

4.2.6 Fabrication of Samples for Submittal to NASA-LBJ Space Center

A total of 2.7 m² (32 ft²) of a rigid polyimide foam 1.0 cm (0.4 in.) thick having a density of approximately 160 kg/m³ (10 lbs/ft³) was delivered to the Boeing Company for fabrication of one 122 x 244 cm (4 x 8 ft) floor panel. The finished panels will be returned to Solar for submittal to NASA-LBJ Space Center in Houston, Texas.

The rigid floor panels were produced by foaming resin E-170-2 modified with 0.5% FC-430 and filled with 10 percent chopped carbon mat. Foaming was done at 287.7°C (550°F) after overnight drying at 82.2°C (180°F). The foam was compressed in a platen press at 287.7°C (550°F) to 1.0 cm (0.4 in.) thickness and trimmed to a size of approximately 56 x 81 cm (22 x 32 in.). The panels are shown in Figure 59.

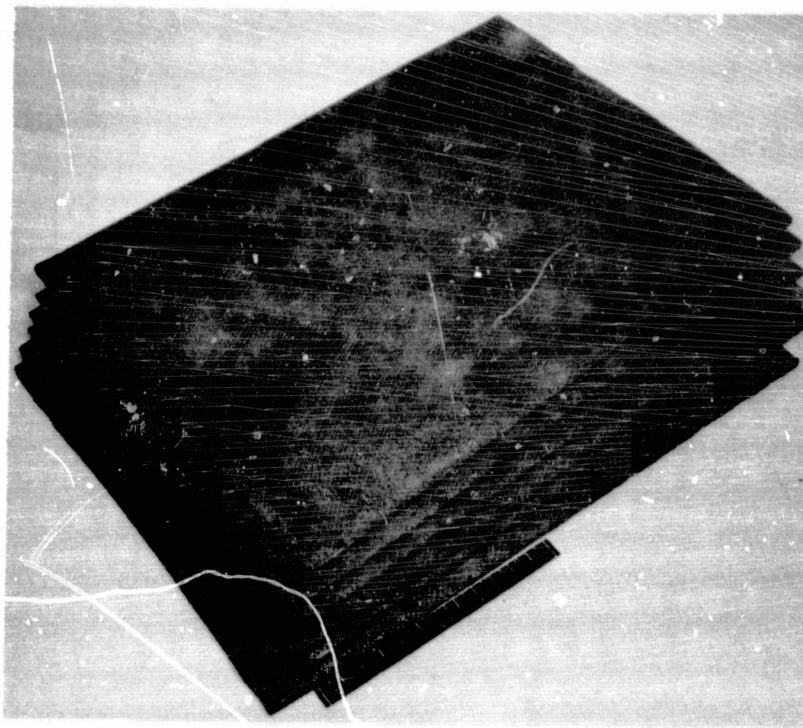


Figure 58a. Carbon Mat Reinforced Rigid Foam Panels; E 170-2

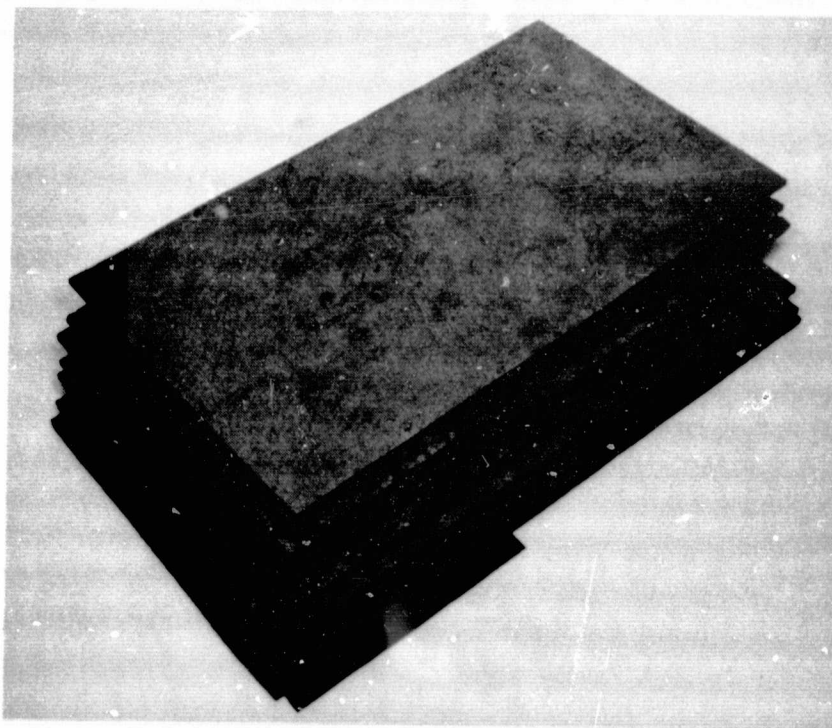


Figure 58b. Foam Filled Honeycomb Panels; FR 160-5

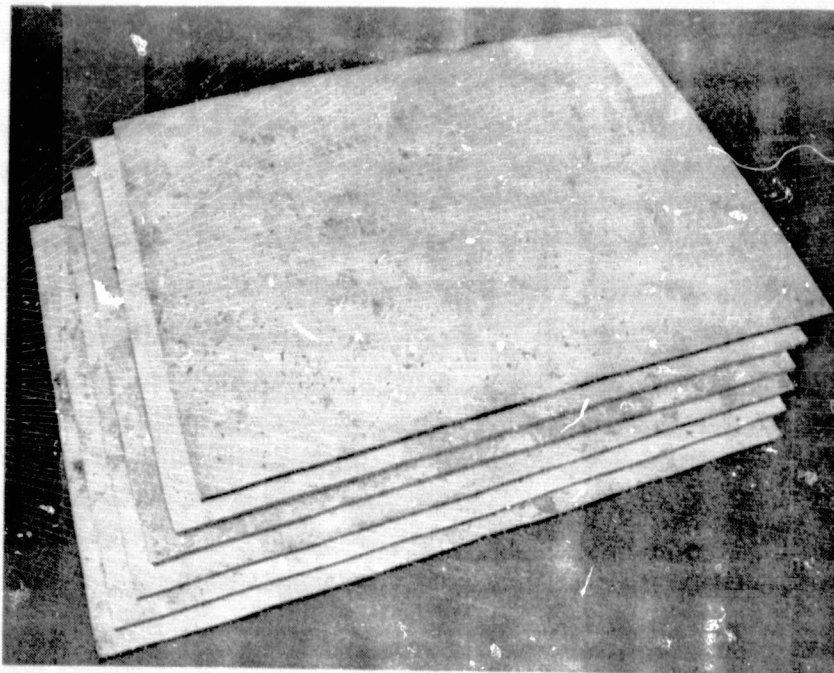


Figure 58c. Chopped Glass Strands Reinforced Rigid Foam Panels; E 170-2

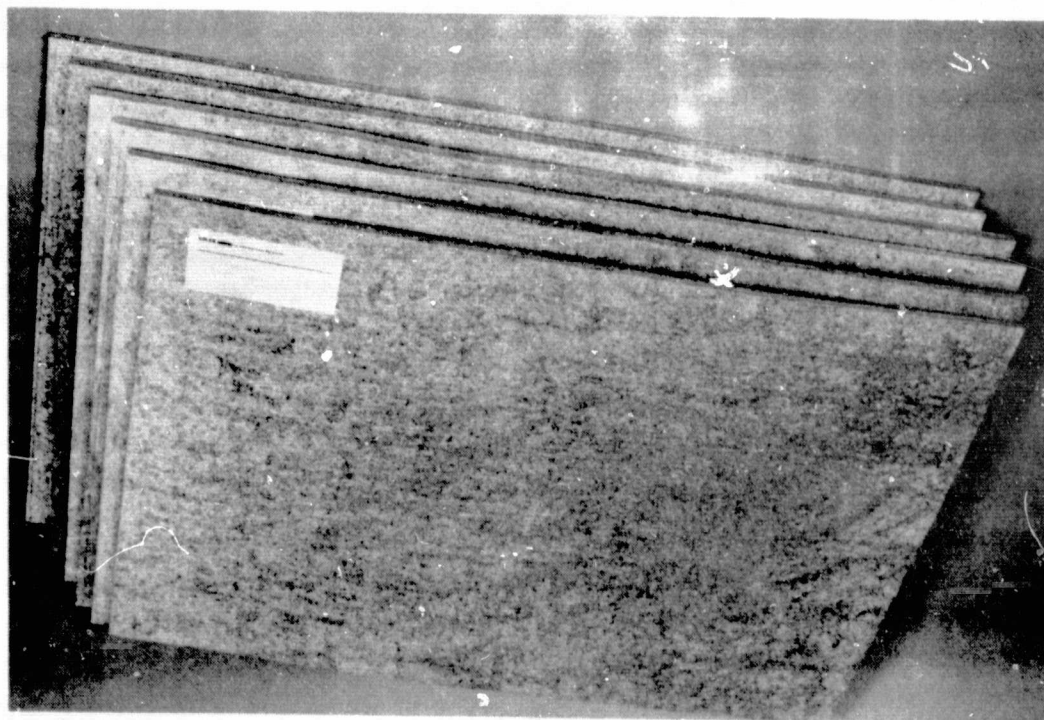


Figure 59. Floor Panels

LAMINATE WALL PANELING

4.2.7 Specimen Preparation and Screening

The work dealing with evaluation and screening of the resins, reinforcements, additives, panel configuration and processing parameters was reported in the previous sections dealing with development of floor paneling. This data is completely applicable to the selection of the candidate systems for fabrication of the wall paneling.

Initial screening of the resins and reinforcements was done on the basis of density only since wall panels must meet significantly lower weight requirements than floor panels. These candidates were further optimized by modification with surface active agents and by improved processing, as it has been reported previously, to select the optimum material and configurations.

On the basis of test data and product evaluation reported in the sections dealing with the development of floor paneling, the following candidates were selected for wall panel applications:

- i. Panel configuration
 - Compressed polyimide foam panels
 - Foam filled honeycombs
- ii. Liquid resin precursors
 - E-170-2
 - E-160-5
- iii. Reinforcements
 - Carbon mat, single layer, 2.5 cm (1 in.) thick
- iv. Surface active agents
 - FC-431

The foam filled honeycomb process was scaled-up to large size panels 55 x 85 x 1.78 (22 x 34 x 0.7 in.) using E-160-5 resin. These panels will be used for fabrication of an aircraft lavatory enclosure which will be tested for fire resistance at NASA-LBJ Space Center test facilities. The compressed polyimide foam was selected as the final candidate for fabrication of the wall panels for testing and for submittal to NASA-LBJ Space Center in accordance with the program plan.

The final wall panel candidate was:

E-170-2 modified with 0.5% FC-431 using 5% carbon mat reinforcement.

A set of seven panels 50 x 80 x 1.78 cm (22 x 32 x 0.7 in.) and one panel 38 x 46 x 1.78 (15 x 31 x 0.7 in.) were fabricated with the above composition and the same procedure used for the floor panels except that the final thickness of the foam was adjusted to 1.78 cm (0.7 in.). The final density of the material was approximately 80 Kg/m³ (5 lbs/ft³) which is 16-24 Kg/m³ (1-1.5 lb/ft³) higher than was obtained with the small scale samples (30 x 20 x 1.78 cm [12 x 12 x 0.7 in.]). Scaling-up problems of this type can be overcome in a continuation of this program by providing a more efficient heat flux through the foaming mass. The panels are shown in Figure 60.

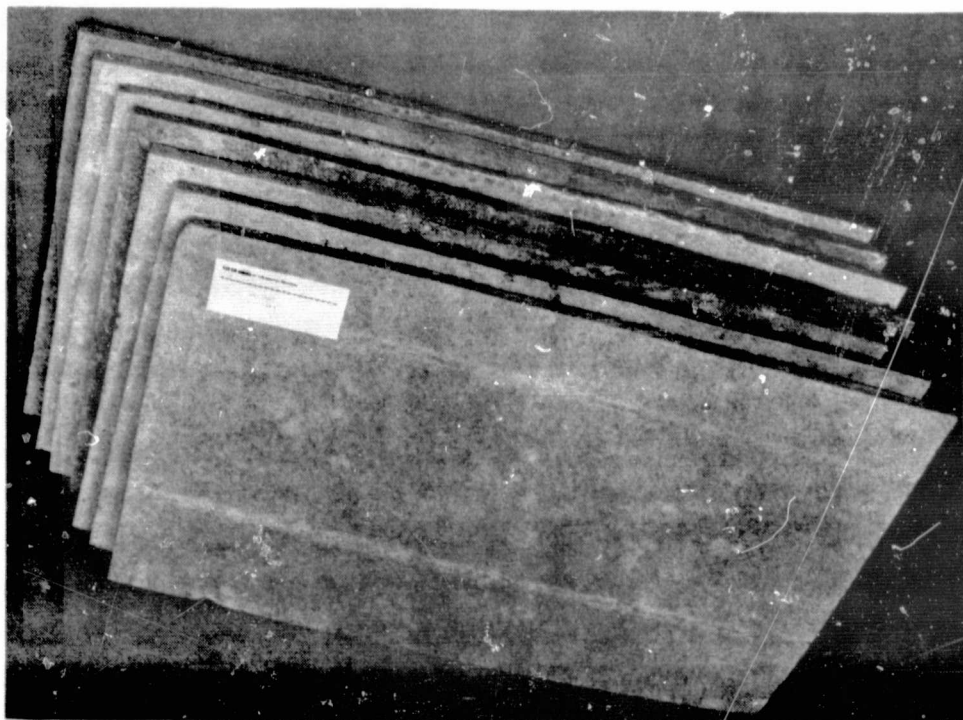


Figure 60. Wall Panels

4.2.8 Fabrication of Wall Panel Samples for Submittal to NASA-LBJ Space Center

The compressed foam rigid panels prepared as reported in the previous section were delivered to the Boeing Company for fabrication of one 122 x 244 cm (4 x 8 ft) wall panel. The finished panel will be returned to Solar for submittal to NASA-LBJ Space Center in Houston, Texas.

4.3 OPTIMIZATION AND CHARACTERIZATION OF THERMAL-ACOUSTICAL INSULATION

This section covers the work dealing with optimization and characterization of sound and heat absorbing open-cell polyimide foams for use as insulating materials in aircraft applications.

Since the thermal-acoustical insulation materials were produced from essentially the same polyimide precursors used for fabrications of flexible resilient foams, this phase of the program was organized to proceed with investigation of the two products as closely as possible in order to benefit from transfer of technology between the two tasks.

The studies undertaken in this phase of the program starts with the synthesis of advanced polyimide precursors (Section 4.3.1) followed by evaluation of foaming methods (Section 4.3.2), fabrication of thermal-acoustical insulation materials and selection of candidates (Section 4.3.3), final characterization (Section 4.3.4) and fabrication of large samples for submittal to NASA-LBJ Space Center (Section 4.3.5).

4.3.1 Advanced Polyimide Synthesis

The work dealing with re-evaluation of the hydrolytic stability of the most promising polyimide foams developed under NAS9-14718, NASA-LBJ Space Center, the selection of the three compositional systems 160, 170 and 190, and the studies of chemical alteration of the three systems with surface active agents, foaming agents and additives was reported in Section 4.1.1 dealing with development of flexible, resilient foams. This data is completely applicable to the selection of candidate resin systems for use in thermal-acoustical insulation. Initial screening was done on the basis of density only and the polyimide precursors selected from among those possessing high molar ratio of 2,6DAP; these have produced foams meeting the density requirements (9.6 kg/m^3 , 0.6 lbs/ft^3). These precursors are:

FR-160-0

FR-190-0

FR-170-1

Optimized systems were attempted by evaluation of the effect of short fibers on the acoustical attenuation properties of the foams. This was done by addition of Fiberfrax (Carborundum) and chopped carbon mat (Union Carbide). The contribution of these two fibers on the physical properties of the foams of system 160-0 modified with 0.2 percent FSB, is reported in Figure 61. At the same level of loading, foams produced with chopped carbon mat have greater degree of porosity and lower density than those produced from Fiberfrax. This data is significant since it provides one more degree of freedom, that of increasing the loading of a fiber known to possess good acoustical attenuation without adversely affecting the degree of porosity and the density of the foams.

This task was organized to include investigation of processes to upgrade the fire hardening properties of conventional fiberglass thermal acoustical insulation since, once impinged by a hot flame, these materials melt and disintegrate. This was attempted by two different methods. These are:

(i) Surface coating

(ii) Surface foaming

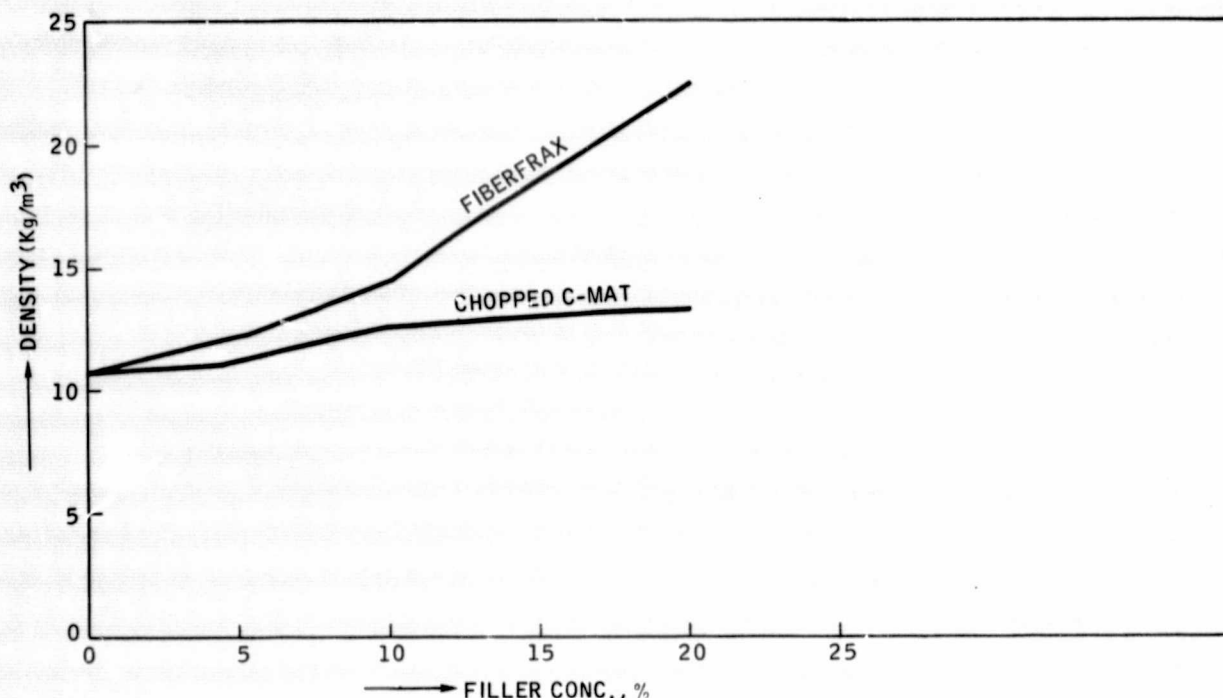


Figure 61. Fillers; Effect on Density of 160-0 Foaming Resin Modified With 0.2% FSB

The first approach was carried out by coating one side of the fiberglass insulation material with a polyimide resin. The material selected for this study was Owens Corning PL105 500W 0.96 cm (0.375 in.) thick fiberglass batting. The resin was applied by brush technique and cured at 315°C (600°F) for 15 minutes. The coating exhibited improved fire hardening properties and, when exposed to a Meker burner, protected the fiberglass batting for four minutes compared to the nude batting which failed after 20 seconds exposure. Difficulties were experienced in producing a homogeneous coating because of the very high surface area and high resin permeability in the fiberglass mat. This problem was overcome by coating the batting by a spray coating process using a DeVilbiss spray gun. This procedure produced a finely dispersed coating on the surface of the glass fibers without resin penetration or agglomeration. The batting exhibited fire-hardening properties, however these properties were greatly dependent upon the resin loading per unit area. This approach proved to be a candidate process for producing fire-hardening acoustical insulation but it will require additional development to optimize the final system.

The second method was carried out by foaming a powder polyimide precursor on one side of the fiberglass batting. Owens Corning fiberglass batting PL105 500W at three different thicknesses, 0.96 cm (0.375 in.), 1.25 cm (0.5 in.) and 2.54 cm (1 in.) was used as the substrate materials. Three different powder polyimide precursors, FR-160-0, FR-170-1 and FR-190-0 were foamed on one side of the batting using thermal processes. The foaming behavior of resins 160-0 and 190-0 were excellent but resin 170-1 exhibited low, non-homogeneous rise. In all cases adhesion to the fiberglass was excellent,

and penetration of the foam in the fiberglass mat was not noticed. Figure 62 shows FR-160-0 resin foamed on 1/2 inch fiberglass batting; total density of the material was 9.6 kg/m^3 (0.6 lbs/ft^3). These foams exhibited fire hardening properties and protected the fiberglass for eight to nine minutes when exposed to a Meker burner.

The work carried out in this phase of the program has clearly demonstrated the feasibility of fabricating new lightweight fire-hardening, foam modified glass batting based upon polyimide technology. Further optimization is required to capitalize this technology and develop it into a stage ready for manufacturing. The effect of this development will be the availability of a new thermal-acoustical insulation material to improve the safety of aircraft.

4.3.2 Foaming Studies and Preliminary Testing

The investigations of new heating methods capable of providing more uniform heat transfer and produce foams with homogeneous cellular structures were reported in Section 4.1.2. This data is completely applicable to the selection of foaming methods for preparation of foams for use in thermal acoustical insulation. Microwave heating proved the most suitable method for foaming all precursors used in fabrication of flexible resilient foams and has been selected as the optimum candidate for thermal acoustical foams. Foams obtained by this method from precursors 170-1 and 170-2 modified with 0.2% FSB possessed the lowest density characteristics ever achieved with any other foaming method or precursor composition. This data has been shown in Section 4.2.1 dealing with foaming studies.

Foams produced by thermal as well as microwave heating met all wicking tests. This data demonstrates that the wicking characteristics of polyimide foams are independent of precursor composition, foaming method, cellular structure, and density.

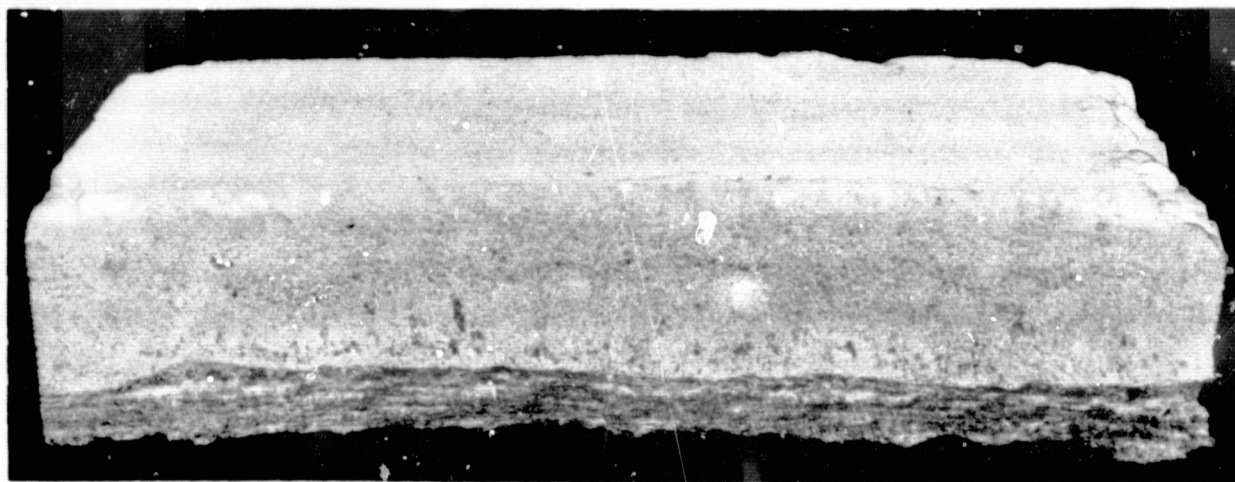


Figure 62. FR 160-0 Foamed on Fiberglass Batting

The acoustical absorption characteristics of the polyimide foams were measured using a Bruel and Kjaer type 4002 impedance tester. The foams selected for testing were those possessing a wide range of cell size and density, and included fiber filled foams modified with various concentrations of surface active agents. The values of the acoustical absorption coefficient varied over a wide range with only a minimum amount of correlation between absorption coefficient, foam structure, density or resin composition. Foam produced by microwave heating produced the most uniform results. Table XXVI presents values of absorption coefficient of fiber filled foams derived from 160-0 precursor and Table XXVII shows values of foams derived from 170 resins at various 2,6DAP ratio.

4.3.3 Preparation of Thermal Acoustical Insulation Materials and Selection of Candidates

The selection of the candidate foam precursors was carried out by foaming the polyimide resins by microwave heating followed by determination of the most critical properties. These were wicking, wetting and density. Resin 190-0 was eliminated previously due to inferior hydrolytic stability (Section 4.1.1). Resin 160-0, 170-1 and 170-2 modified with 0.2% FSB produced foams meeting all the requirements listed above.

Owens Corning fiber glass batting modified by coating or by foaming techniques was not included in the list of candidates since additional work was required to optimize the processes and compositions. Although carbon and Fiberfrax fibers produced foams with the best absorption coefficient, these could not be produced by microwave foaming since the fibers interacted with the high frequency radiation causing localized overheating during foaming. Thus these compositions were eliminated from this study.

The overheating of the fiber filled foams under the high frequency field may be of significance in a continuation of this program to evaluate foaming and curing of polyimide resins in a single step. The additional energy necessary to increase the temperature of the foaming mass to the temperature needed for the condensation reaction (287.7°C, 550°F) would evolve from the interaction of the fibers or fillers with the microwave field. This interaction has shown to be so high to cause carbonization of many polyimide foams produced by microwave heating. The work carried out thus far has demonstrated the feasibility of this technique, but more effort is necessary to develop a safe, efficient process. The immediate results from the realization of this concept will be a foaming cycle of a duration of a few minutes, and foams with the most uniform cell structure and the lowest product cost.

Precursor 170-2 modified with 0.2% FSB was selected as the optimum candidate for use in thermal acoustical insulation. This selection was based on the data presented in this and in previous sections, and on cost considerations. This resin has the lowest raw material cost in view of its low molar ratio of 2,6DAP. This resin was used to fabricate samples for testing and for submittal to NASA-LBJ Space Center as will be discussed next.

Table XXVI
Absorption Coefficient of Foams Derived From 160-0 Precursors

Resin Number	Additives/Fillers	Density kg/m ³	Average Absorption Coefficient 2000 Hz
Owens Corning PL105 500W		10.9	0.970
160-0	None	7.1	0.943
160-0	5% Fiberfrax	8.3	0.947
160-0	10% Fiberfrax	11.0	0.950
160-0	20% Fiberfrax	19.1	0.835
160-0	5% chopped carbon mat	7.1	0.941
160-0	20% chopped carbon mat	13.1	0.878

Table XXVII
Absorption Coefficient of Foams Derived From 170 Precursors

Resin Number	2,6DAP Ratio	Additives/ Fillers	Density kg/m ³	Average Absorption Coefficient 2000 Hz
Owens Corning PL105 500W	-	--	10.9	0.970
170-0	0.5	0.2% FSB	9.3	0.938
170-1	0.4	0.2% FSB	7.5	0.784
170-2	0.3	0.2% FSB	7.1	0.778
170-5	0.2	0.2% FSB	6.4	0.858

4.3.4 Final Characterization of Thermal Acoustical Insulation Material

The characterization of the final candidate was conducted using samples produced by foaming the 170-2 resin modified with 0.2% FSB using microwave heating techniques. Summary of the results is given in Table XXVIII.

4.3.5 Fabrication of Large Samples for Submittal to NASA-LBJ Space Center

Polyimide foam slabs having approximate dimensions of 38 x 38 x 7.6 cm (15 x 15 x 3 in.) were produced by spreading a 1.0 cm (0.4 in.) thick layer of 170-2 polyimide foam precursor modified with 0.2% FSB over an area 38 x 38 cm (15 x 15 in.) on a Teflon sheet (0.16 cm, 0.062 in. thick). Foaming was carried out in the microwave oven for 5 minutes followed by post curing at 260°C (500°F) for one hour. The outer skin was removed and the foam cut to size. The density of the foam was less than 8 Kg/m³ (0.5 lb/ft³). A total of 3.6 m² (4.4 yd²) of the final product was produced at a thickness of approximately 7.6 cm (3 in.). These samples will be delivered to NASA-LBJ Space Center in Houston, Texas.

4.4 INVESTIGATION OF PROCESSES FOR HIGH STRENGTH POLYIMIDE MOLDED SHAPES

This phase of the program describes the work relevant to the development of processes for heat forming or molding polyimide compositions into high density interior aircraft components to replace conventional, more flammable materials.

Molding methods used to shape polyimide resins have been limited in the past to high temperature compression techniques and to fabrication of small components due to the poor flow characteristics of these resins. The process selected for fabrication of the high strength polyimide molded shapes under study in this phase of the program is based on heat-forming the rigid panels, described in Section 4.2, using compression techniques.

The studies of this phase of the program start with selection of the polyimide precursors and resin reinforcements (Section 4.4.1), followed by preparation and evaluation of molding hardware (Section 4.4.2) and fabrication of prototype molded shapes (Section 4.4.3). The most promising candidates are then optimized by investigation of methods to produce decorative effects (Section 4.4.4) followed by advanced testing (Section 4.4.5), and fabrication of final samples for submittal to NASA-LBJ Space Center (Section 4.4.6).

Table XXVIII
Summary of Results. Thermal Acoustical Insulation
170-2 Resin 0.2% FSB

Property	ASTM Method	Units	Goal	Actual
Density	D-1564	Kg/m ³ lbs/ft ³	9.6 0.6 max.	5.6 0.35
Breaking Strength	CCC-T-191	N/m lbs/in.	175.1 1.0 min.	744.2 4.25
Wicking as received	Water immersion	cm in. precipitate	1.0 max 0.25 max None	None detectable None detectable None detectable
Wicking after oven drying 71.1°C (160°F)	Water immersion	cm in. precipitate	1.0 max. 0.25 max. None	None detectable None detectable None detectable
Flexibility		deterioration after bending on one-foot radius	None	None detectable
Corrosion (Aluminum)		Pitting	None	no pitting)
Elevated Temperature Resistance		Weight loss	15 mg max.	12 mg (water)
Oxygen Index	D-2865	% oxygen	40 min.	45
Smoke Density DS Uncorrected	NBS	Optical Density	30-50 max.	2.0
Verticle Bunsen Burner Test, 60 seconds		Flame Time seconds	10 max.	0
		Burn length cm in.	15 max. 6 max.	3.0 1.2
		Dripping		None detectable
1000°C (2014°F) Flame Test (Meker Burner) 10 minutes		Cold Face Temp. °C °F	260 500	142 288
Vibration		1 Hr 30 Hz 5 cm amplitude	No damage	None detectable
Acoustical Properties		Absorption Coefficient 1000 Hz 2000 Hz 4000 Hz	0.736* 0.965* 0.916*	0.533 0.949 0.737
*Owens Corning PL 105 500W				

4.4.1 Selection of Polyimide Precursors and Resin Reinforcements

The work dealing with screening and selection of candidate polyimide precursors for the three compositional systems 160, 170 and 190 and that dealing with evaluation of fillers or reinforcements by determination of their contribution to the mechanical properties was reported in Section 4.2 covering the development of floor and wall paneling. This data is completely applicable to the selection of candidate resin systems for use in fabrication of high strength molded shapes.

On the basis of test data and product evaluation derived from the study of rigid panels, the liquid resin precursors E-170-2 and E-160-5 were selected. These resins were used to prepare the rigid panels as reported in Section 4.2. The panels were then molded into high strength shapes by the process described in Section 3.7 and finally tested for the most critical properties. Impact strength was selected as the most critical property since polyimide resins molded by conventional compression techniques have shown to be deficient in this respect. Resin E-170-2 was selected for this study. The results of these tests are shown in Table XXIX for compositions made at a filler concentration of 15 percent based on polyimide solids. Nomex fibers produced the most significant contribution to strength.

The evaluation of the effect of filler concentration upon the impact strength of the molded panels was carried out next using resin E-160-5 and Nomex fibers. The data of Table XXX shows that a direct relationship exists between fiber concentration and impact strength. Maximum strength values were obtained at Nomex concentration in the range of 15-16 percent. Higher Nomex fibers loadings were not possible due to resin starvation. To find means to improve the impact properties of the most promising compositions, molded parts were produced by compressing rigid panels between two layers of polyimide coated woven fabric. The process yielded finished molded shapes with a reinforcing (or decorating) skin on both sides of the panels. The coated fabrics were prepared as will be described in Section 4.5 and included:

- Nomex paper 2.5 mm thick (10 mil)
- 181 A-1100 woven glass fabric - Thalco
- 120 A-1100 woven glass fabric - Thalco
- Asbestos cloth, type Novatex, Raybestos-Manhattan

These configurations had no effect on the impact strength indicating that this property is almost entirely a function of the composition of the material.

A new reinforcement which had previously shown to permit higher fiber loadings in fabrication of conventional polyimide molding resins was tested next. This reinforcement is chopped glass strands. This study was designed to offer an assessment of the relative strength of molded panels prepared from low cost, readily available inorganic fibers. Preliminary experiments proved the feasibility of the concept and produced molded parts with significantly higher Izod impact strength. This lead to a comprehensive

Table XXIX
Izod Impact Strength of Molded E 170-2 Compositions

Filler	Impact Strength	
	ft-lb/inch	J/m
Chopped Carbon Mat	0.39	20.8
Graphite Fibers	0.78	41.5
Carbon Fibers	0.43	23.0
Fiberfrax	0.54	28.7
Nomex	1.73	92.5
Kevlar	1.63	87.0
Carbon Mat	0.58	31.0

Table XXX
Nomex, Effect of Concentration on Impact Strength of
Molded E 160-5 Compositions

Nomex Concentration Parts/100 Parts Solid Resin	Impact Strength	
	ft-lb/inch	J/m
2.6	1.09	58.0
5.2	1.01	53.8
7.8	1.17	62.3
10.5	1.79	95.4
13.1	1.90	101.2
15.7	2.25	119.9

evaluation of the system starting with the effect of glass concentration on the properties of the molded parts. This study was conducted using resin E-170-2 and 1.25 cm (0.5 in.) long glass strands treated with 832 binder. The glass was compounded into the liquid resin using a mechanical mixer and the mixture spread over aluminum foil at a solid loading of 1.42 g/cm². After drying in an oven to remove the solvent, the resin was foamed at 287.7°C (550°F) for 30 minutes and compressed at 287.7°C (550°F) and 394-689 kPa (50-100 psi) in a platen press. Table XXXI shows physical and mechanical values obtained by testing the various compositions made at a glass strands concentration of 5 to 60 percent based on total solids.

Table XXXI
Chopped Glass Strands; Effect of Concentration on Properties
of Molded E 170-2 Compositions

Glass Strands Concentration %	Density		Izod Impact Strength	
	lbs/ft ³	kg/m ³	ft-lb/in.	J/m
5	48.3	772.8	1.57	83.6
10	65.0	1040.0	1.57	83.6
20	72.8	1164.8	2.15	114.6
30	83.5	1336.0	4.93	262.7
40	85.9	1374.4	8.79	468.5
50	96.7	1547.2	9.13	486.6
60	100.6	1609.6	6.40	341.1

As proved for the Nomex filled systems, a direct relationship exists between glass concentration and impact strength. In these experiments glass loadings of up to 60 percent were possible and no resin starvation was experienced. Compositions containing 40 to 50 percent chopped glass strands met the goal established for impact strength and density characteristics.

4.4.2 Preparation and Evaluation of Molding Hardware

The preliminary tooling used for compressing the rigid panels to high strength material consisted of two 6061 type aluminum plates 30.5 x 30.5 x 0.625 cm (12 x 12 x 0.25 in.). This rather primitive hardware was sufficient to produce specimens for Izod impact testing. A release agent, MS 136 Fluorocarbon, was applied to the surfaces of the plates to prevent sticking. The first task of this effort involved the study pertinent to the effect of density on the impact strength. This investigation was carried out with

E-160-5/Nomex (5 cm, 2 in.) compositions at a fiber concentration of 10 percent based on polyimide solids. This data is shown in Figure 63. The range of density was obtained by preparing rigid panels at increasing loading per unit area, followed by compressing to the same thickness. Therefore, the density of the final part was achieved by the use of higher mass per unit area. Using these process conditions the impact strength of the material decreased with an increase of density. Conversely, when the density was obtained by compressing the same resin/filler composition to different thicknesses, the impact strength of the material increased with an increase of density but started to decrease when resin sintering began to occur and reached the lowest level when fully sintered molded parts were obtained. This data is shown in Table XXXI. The point of maximum impact strength has been identified as the transition point at which the resin, which is predominantly in the high density foam stage, shows signs of sintering.

The data obtained in this study has been sufficient to assess the contribution of the most important molding parameters and for gathering data for fabrication of more advanced hardware. This was accomplished by fabricating a mold from low carbon steel. The mold consisted of a square cavity 15.3 x 15.3 cm (6 x 6 in.) with the four corners rounded to a 0.635 cm (0.25 in.) radius, having a depth of 5.1 cm (2.5 in.). Two plates, 3.8 cm thick (1.5 in.) inserted in the cavity formed the top and bottom enclosures of the mold. This tooling is shown in Figure 64.

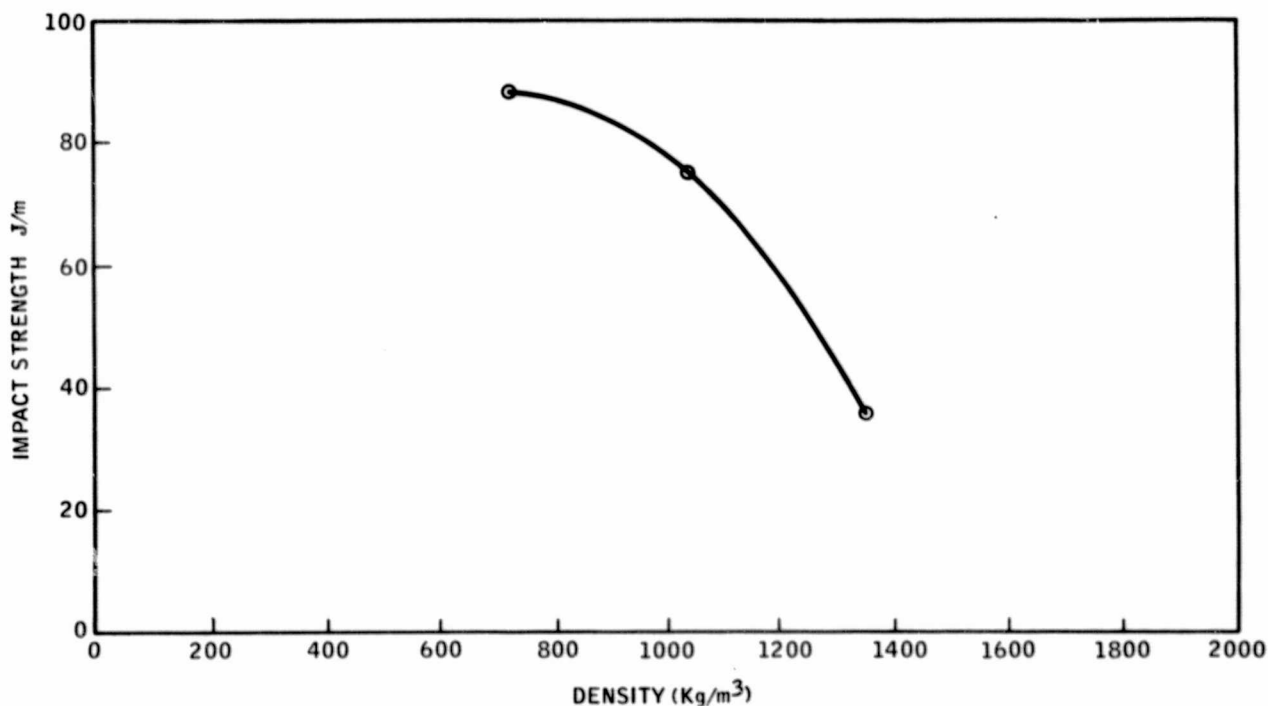


Figure 63. Density; Effect on Impact Strength of 160-5 Nomex Molded Shapes

Table XXXII
Density; Effect on Impact Strength of 160-5
Nomex Molded Shapes

Sample No.	Density		Impact Strength	
	Kg/m ³	lb/ft ³	ft-lb/in.	J/m
1	366	22.8	1.13	60.2
2	702	43.8	0.97	45.3
3	745	46.5	1.10	58.6
4	976	61.0	1.64	87.4
5	1060	66.2	1.44	76.7
6	1364	85.2	0.625	33.7

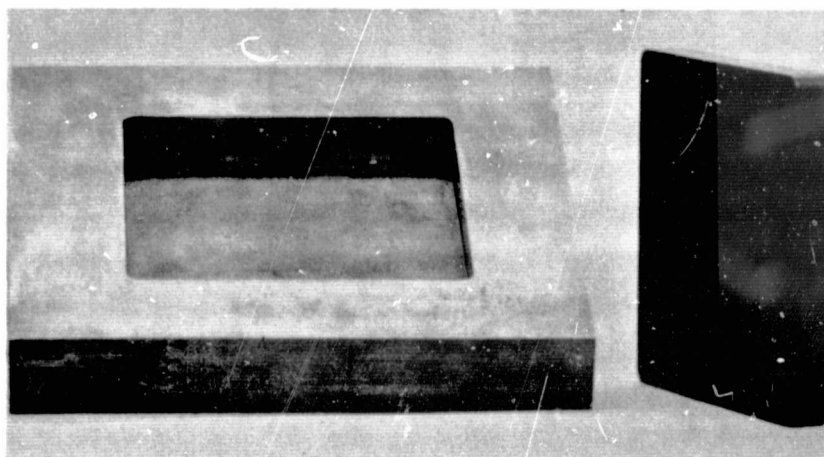


Figure 64. Mold Configuration

The resin compositions under study have shown to possess sufficient flow characteristics for obtaining simple geometrical shapes such as food trays. A study of size and shape limitations, however, was not carried out. Further optimization and process development will be required in future programs to upgrade this technique for achieving more complex geometrical components for use in a variety of interior aircraft applications.

4.4.3 Prototype Molded Shapes by Compression Techniques

This first task of this study involved modification of the mold configuration shown previously to permit easier opening. This was accomplished by machining the inserts with less tight dimensions (1.56 mm, 0.063 in. gap). The problem experienced with sticking was next studied. Conventional mold releases, such as MS 136 (Miller Stephenson Chemical Co., Inc.) were found to be ineffective. Thoughts were given to hardening the surfaces of the mold by chrome plating or by the use of superalloy materials; these studies will be undertaken when optimization of the system is continued in future programs dealing with development of manufacturing capabilities. The problem was overcome by protecting the surfaces of the mold with aluminum foil coated with MS 136 release agent; the foil was then peeled off the molded part without difficulty. This crude technique was found to be adequate for fabrication of prototype test specimens.

The study of molding parameters was carried out next. Several experiments were conducted to determine an optimum molding process using an electrically heated platen press. The following procedure was established using the mold configuration shown previously. The mold was heated to 315°C (600°F) and the rigid foam composition placed in the cavity and heated for 15 minutes. Pressure was applied and the part held in compression for 15 additional minutes at 315°C (600°F). The mold was then cooled to 232°C (450°F) with the part still under compression; the pressure was released and the molded part removed. The pressure necessary to achieve a density of 1100-1600 kg/m³ (68-100 lbs/ft³) with 40-50 percent glass strands loading was approximately 17.2×10^2 kPa (250 psi).

4.4.4 Investigation of Methods to Produce Decorative Surface Effects

This task involved a feasibility study of techniques to produce molded components meeting the decorative and functional characteristics of present aircraft interior paneling. The most common method to achieve decorative effects in interior aircraft involves lamination of Tedlar, Kynar or other protective films. This technique was used in this program by bonding Tedlar on the flat molded panels using conventional epoxy adhesives. This proved the feasibility of the process. The other methods attempted involved the direct coating with a pigmented polyimide resin and the use of polyimide coated fabrics. The pigmented coating and the coated fabrics used in this study were those developed in Section 4.5 which will be discussed next. Coating techniques proved successful but required molded parts free from surface imperfections and worked only on non-porous material. Decorative effects by bonding polyimide coated fabrics produced only marginal results due to stiffness of the fabrics.

The objective of this effort involved investigations of alternative methods for producing decorative effects on molded parts. This objective was achieved but it will require additional effort to develop these techniques into processes readily applicable to decorate molded parts, preferably in a one step molding and lamination process.

4.4.5 Advanced Testing

The characterization of the optimum candidate was conducted using samples heat-formed in the mold configuration shown previously. The samples were prepared from 40 percent chopped glass strand filled E-170-2 resin in accordance with the process described in Section 3.7. Summary of the results is given in Table XXXIII.

Table XXXIII
Summary of Results - Molded Shapes

Property	ASTM Method	Units	Goal	Actual
Specific gravity	D792	g/cc	1.0-1.5	1.23
Tensile Strength	D-638	psi n/m ²	8000-12,000 55.1 x 10 ⁶ - 82.7 x 10 ⁶	6866 47.3 x 10 ⁶
Elongation	D-638	%	4-8	1.1
Impact Strength	758-48	ft-lb/in. J/m	7-12 374-640	7.3 390
Heat Distortion Temperature (264 psi)	D-648	°C °F	148.9-176.7 300-350	Higher than: 204.4 400
Rockwell Hardness (Alpha)	D-785		R110-R130	R102
Oxygen Index, LOI	D-2863		40 minimum	60
Smoke Density D _s uncorrected	NBS		30-50	1.0
TGA	-	°C °F	Stable to: 204.4 400	400 752

4.4.6 Fabrication of Molded Samples for Submittal to NASA-LBJ Space Center

A total of 0.85 m² (one square yard) of molded samples were produced by heat-forming a 40 percent chopped glass strand filled E-170-2 resin in an electrically heated platen press at a temperature of 315°C (600°F) and 34 x 10² kPa (500 psi) for 15 minutes. The parts were cooled to below 232°C (450°F) and removed. The tooling used for obtaining the flat sheets consisted of two low carbon steel plates. The flash was removed on a grinding wheel and any edges cut off on a bandsaw. These samples will be delivered to NASA-LBJ Space Center in Houston, Texas.

4.5 OPTIMIZATION OF FLEXIBLE POLYIMIDE COATED FABRICS

This phase of the program covers the work dealing with optimization of processes to upgrade open weave or knitted fabrics with polyimide resin compositions having attributes as protective coatings to obtain decorative effects and fire-hardening properties of the fabrics.

The effort of this task starts with evaluation of selected fabrics for compatibility with the resin systems (Section 4.5.1) followed by investigation of processes to produce decorative effects (Section 4.5.2). The selected fabrics and resin systems are then further optimized by selecting optimum processes for producing samples for testing (Section 4.5.3) and for submittal to NASA-LBJ Space Center (Section 4.5.4).

4.5.1 Evaluation of Fabrics

The polyimide coatings used for this application are based on a new technology, previously developed, which permits preparing readily soluble polyimide resins capable of undergoing polymerization by an exchange reaction rather than by the conventional condensation and cyclization mechanisms. The advantages of this new technology is especially important in coating applications where a variety of solvents, pigments, fillers or additives are required to achieve specific coating properties. The most important characteristic of the coatings is the improved adhesion to most substrates, including glass.

The initial effort of this task involved preparation of selected resin compositions for use in evaluation of the fabrics. These resins were:

GG-12
GG-14
GG-15

The resins were prepared in a solvent, which was a mixture of dimethyl formamide, acetone and methyl ethyl ketone and used in the initial evaluation of the fabrics without the addition of fillers or pigments.

The fabrics selected for the evaluation were:

Style 181, A-1100 finish satin weave glass fabric, Thalco
Style 120, A-1100 finish satin weave glass fabric, Thalco
Style 28 PO67N Asbestos cloth, type Novatex, Raybestos Manhattan
Type 0200A tire roving, Owens Corning
Nomex paper 0.5 mm (2 mil) thick, Dupont
Nomex paper 2.5 mm (10 mil) thick, Dupont

Table XXXIV shows the physical properties of fabrics coated with the selected resins. The coatings on glass fabrics were the most homogeneous and possessed good flexibility and good adhesion. The adhesion of the coatings to the asbestos cloth was marginal and flexibility of the fabric poor. A lower curing temperature in the range of 250°C (450°F) improved both adhesion and flexibility of the asbestos cloth. Nomex paper 0.5 mm (2 mil) thick showed tendency to embrittlement while 2.5 mm (10 mil) thick Nomex was not affected by the processing conditions.

Table XXXIV
Coated Fabrics - Coating Physical Properties

Fabric/Substrate	GG Resin	Flexibility Test		Tape Adhesion Test % Removal	Color/Appearance
		90° Bend	180° Bend		
Woven Glass 120-A1100	12	Pass	Fail	0	Brown, homogeneous coating
Woven Glass 120-A1100	14	Pass	Pass	0	Yellow, homogeneous coating
Woven Glass 120-A1100	15	Pass	Pass	0	Yellow, homogeneous coating
Woven Glass, 181-A1100	12	Pass	Fail	0	Brown, homogeneous coating
Woven Glass, 181-A1100	14	Pass	Pass	0	Yellow, homogeneous coating
Woven Glass, 181-A1100	15	Pass	Pass	0	Yellow, homogeneous coating
Woven Asbestos, Novatex	12	Fail	Fail	10	Brown, homogeneous coating
Woven Asbestos, Novatex	14	Pass	Pass	3	Yellow, homogeneous coating
Woven Asbestos, Novatex	15	Pass	Pass	0	Yellow, homogeneous coating
Nomex Type 410, 2 mil	12	Fail	Fail	0	Brown, homogeneous coating
Nomex Type 410, 2 mil	14	Fail	Fail	0	Brown, homogeneous coating
Nomex Type 410, 2 mil	15	Fail	Fail	0	Brown, homogeneous coating
Nomex Type 410, 10 mil	12	Pass	Pass	0	Brown, homogeneous coating
Nomex Type 410, 10 mil	14	Pass	Pass	0	Brown, homogeneous coating
Nomex Type 410, 10 mil	15	Pass	Pass	0	Brown, homogeneous coating

The tire roving, Owens Corning type 0200A, was not compatible with the process and with the coating resins as evidenced by embrittlement and poor coating adhesion.

Vertical and horizontal fire tests were performed on the coated fabrics. The materials possessed fire hardening properties and did not produce detectable quantities of smoke during combustion, with the exception of coated Nomex paper which resulted in improved, but still marginal properties for use in fire-hardening applications.

Two new materials were tested at the end of this task. These were Mannitemp 111 and Mannitemp 115, two glass/asbestos compositions manufactured by the Manning Paper Co. These materials were compatible with the polyimide coatings and produced flexible and fire resistant materials.

4.5.2 Investigation of Decorative Effects

Direct coloring techniques with this type of resin have been demonstrated previously and used on aluminum and steel substrates. GG-12 resin was selected for this study. Coloring was accomplished by milling Phthalo Blue G BT 4693, a phthalocyanine blue pigment, on a ball mill and by coating the fabrics reported previously with the exception of 0.5 mm (2 mil) Nomex paper which was excluded. Figure 65 shows a coated, fully cured asbestos fabric.

These coatings were tested in accordance with the same schedule reported in Table XXXIV with the following results.

All coatings were uniform without visible flaws or striations.

All coatings on fiberglass met bending and tape test adhesion; coatings on asbestos cloth were marginal.

The flexibility of the decorative coatings on fiberglass appeared to be better than that obtained with the base resin only.

The coatings met the Meker burner test and possess fire hardening properties.

Experiments were also conducted aimed at producing coated fabrics by foaming, as opposed to coating, a polyimide resin on one surface of the fabrics. The objective of this effort was to produce a flexible material simulating synthetic leather. This was accomplished by foaming FR-160-5 and FR-170-1 on 181 and 120 A-1100 finish satin weave glass fabrics and woven Ryton SN 424-150 followed by compressing the foams to a thickness of approximately 0.625 cm (0.25 in.) or by bonding sheets of preformed polyimide foams on the surface of the fabrics using Scotch-Weld 2216 B/A epoxy adhesive. Small prototype samples were produced and submitted to NASA-LBJ Space Center. This preliminary work has clearly demonstrated the feasibility of fabricating new light weight, non-flammable laminated foam materials, but this technology requires further development in a continuation of this program.

4.5.3 Preparation of Coated Fabrics for Testing

The initial task of this phase of the program was a study of coating processes. This was carried out by coating 181 style satin weave glass fabric with a new pigmented polyimide composition by the following methods; spray coating, dip coating, roll coating. The criteria of selection of the optimum method was based upon uniformity of the coating and flexibility of the fabric. The new pigmented polyimide resin was prepared by milling Yellow Fast R GT 8105-GG-12 compositions on a ball mill.

Dip and roll coating processes produced irregular coating thickness and striations; these methods are more adaptable to continuous large scale production. Spray coating was done using a DeVilbiss spray gun with a fluid tip D by the procedure described in Section 3.8. Coatings produced by this



Figure 65. Coated Asbestos Fabric

process were uniform and flexible. This method was selected for preparation of the samples for testing. Test specimens were prepared at a coating thickness of 0.075 mm (3.0 mil) and 0.125 mm (5.0 mil). These samples were tested by the U.S. Testing Laboratory in Los Angeles, California and the results reported in Table XXXV.

Table XXXV
Summary of Results - Coated Fabrics

Property	ASTM Method	Units	Goal	Actual	
				#2 3.0 mil	#3 5.0 mil
Specific Gravity	D-792	g/cc	1.0-1.5	0.95	0.96
Bursting Strength	D-751-68	kPa psi	275 minimum 40 minimum	3000 436	2040 296
Abrasion Resistance	FTMS 1916		250 cycles no loose fibers	200**	250
Blocking	FTMS 191		not higher than 3	1	1
Flex-Crack Resistance	D-2176-69		5000 cycles	890	477
Stiffness	FTMS 1916	cm in.	2.5 minimum 1.0 minimum	22.3 8.8	24.6 9.7
Coating Adhesion*	D-3002-71	% coating removed	0	0	0
Oxygen Index, LOI	D-2863		40 minimum	60	60
Smoke Density	NBS		30-50	1.0	2.0
D _s (uncorrected)					
TGA	-	°C °F	Stable to: 204.4 400	400 725	
<p>*T-Peel test for adhesion was not possible for this type of material. 1.</p> <p>**Fabric worn out.</p>					

4.5.4 Fabrication of Samples for Submittal to NASA-LBJ Space Center

A sample having an area of approximately 1.67 m² (2 yds²) was prepared by spray coating Style 181, All100 finish satin weave glass fabric with GG-12 polyimide resin pigmented with Yellow Fast R GT 8105. The coated fabric was dried at 93°C (200°F) for 30 minutes and cured for 1 hour at 149°C (300°F) and 2 hours at 232.2°C (450°F). The sample will be delivered to NASA-LBJ Space Center in Houston, Texas.

5

RECOMMENDATIONS FOR FUTURE WORK

The technology developed to produce the polyimide materials under study in this program has provided the basis for small scale pilot plant processes which have been used to fabricate the final test specimens. These processes have been found to be deficient with respect to size effects and require additional effort to optimize and develop the products to large scale production. The following suggestions are recommended.

The optimization of the flexible, resilient foams requires the use of a microwave oven with higher power outputs and modification of the resin system to maintain mechanical properties as the foam size is increased. The addition of fillers capable to interact with the microwave field will provide additional energy for the foaming process. A comprehensive study to define the relationships between foam density and mechanical properties will be undertaken. This will be done to select final optimized process parameters to achieve uniform foam quality before initiation of large scale production.

Considerable technology transfer will occur between this task and that dealing with scale-up of thermal acoustical insulation materials, although the latter is less sensitive to size effects. The effect of short fibers on the acoustical properties of selected foams will be further evaluated since this concept has shown to contribute to improved acoustical properties. This concept was, however, abandoned due to incompatibility of the fibers with the high frequency field. The fire-resistance of conventional thermal acoustical insulation will be upgraded by modification with polyimide coating or foaming. The objective of this task will be to improve the fire hardening properties of the fiberglass by processes which are readily adaptable to large scale production. The work carried out in this program has clearly demonstrated the feasibility of these techniques.

The technology dealing with the one-step fabrication of wall panels with hard dense skins and low density core requires considerable resin and process development to select candidates for large scale production. Immediate results from this effort will be the development of rigid low density wall panels ready to be laminated with decorative skins.

The fabrication of high strength compressed foam panels will be carried out by using polyimide resins filled with micro or macroballoons and other selected fillers. Foam filled honeycombs will be modified with microballoons or fillers to provide better heat hardening properties. Nude honeycomb materials will also be evaluated in attempting to improve the fire resistance of the Nomex by simultaneous coating-foaming processes. Compressed foam panels with improved load bearing characteristics will be investigated and evaluated.

To overcome the present deficiencies in the area of bonding agents for fabrication of finished floor and wall paneling, polyimide adhesives will be developed and modified to provide edging and potting compounds. The same technology will be adapted to produce electrical coating to protect wires, cables, circuits and other conductors used in aircraft applications.

Processes to produce molded parts by low temperature heat forming processes will be evaluated. These components will be produced by the use of new polyimide compositions which undergo sintering at lower temperature and may yield transparent molded polyimide parts for special aircraft applications. Prototype hardware will be fabricated by compression molding techniques to produce selected components presently used in interior aircraft. This task will be carried out using surface hardened mold configurations obtained by plating or by fabricating the mold from superalloy materials. Evaluation of the techniques to produce molded components meeting decorative requirements will be continued using coating or lamination methods. The ultimate objective of this task is to develop these techniques into a one-step molding and lamination process for large scale manufacturing. Finally new methods of producing light weight non-flammable laminated polyimide foam materials simulating synthetic leather will be developed. These methods will utilize polyimide powder resins which can be plasticized and foamed on suitable substrates to produce foam coated fabrics to replace conventional more flammable materials presently used in aircraft interior, such as seat arm rest, trash can liners, curtains and similar articles. The fabrication of these materials will also be attempted by bonding preformed sheets of polyimide foams on suitable substrates using adhesive systems selected for low-smoke emittance and low flammability characteristics.

REFERENCES

1. Gagliani, J., "Fire-Resistant Resilient Foams", Final Report submitted to National Aeronautics & Space Administration, Houston, Texas, NAS9-14718.